63-3-5

OFFICE OF NAVAL RESEARCH

Contract Nonr 220(26)
Task No. NR 055-388

TECHNICAL REPORT NO. 21

Nuclear Magnetic Resonance Spectroscopy. Cyclopropane Derivatives.

Dinshaw J. Patel, M. E. H. Howden and John D. Roberts

Prepared for publication
in the
Journal of the American Chemical Society

California Institute of Technology
Division of Chemistry and Chemical Engineering
Pasadena, California

April 1963

[Contribution No. 2964 from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California]

Nuclear Magnetic Resonance Spectroscopy. Cyclopropane Derivatives.[1]

---

[1] Supported in part by the Office of Naval Research and the National Science Foundation.

By Dinshaw J. Patel,[2] M. E. H. Howden and John D. Roberts

---

[2] J. N. Tata Fellow, 1961-1963.

Chemical shifts and coupling constants have been determined from the analysis of proton nuclear magnetic resonance spectra for a series of cyclopropane derivatives. The geminal and vicinal cyclopropyl couplings have opposite signs. Additional ^{13}C-H coupling constants have been obtained for cyclopropanes which support the conclusion that the hybridization of the carbon bonding orbitals in cyclopropanes is close to sp^2. The chemical shifts for several cyclopropane hydrocarbons seem consistent with a ring-current effect.

Proton n. m. r.[3] and fluorine n. m. r.[4] spectroscopy have been

---

[3] G. L. Closs, R. A. Moss and J. J. Coyle, J. Am. Chem. Soc., **84**, 4985 (1962).

[4] W. Mahler, J. Am. Chem. Soc., **84**, 4600 (1962).

utilized for structure determinations of substituted cyclopropanes. Coupling constants and chemical shifts of cyclopropane derivatives[5,6] have recently been reported and interpreted in terms of substituent effects and molecular geometries.[6]

In the present research, the spin-spin splittings in the proton n.m.r. spectra of several substituted cyclopropanes have been analyzed using standard methods[7,8] with results shown in Table I.

The Wiberg,[9] the Bothner-By and the Swalen[10] computer

---

(5) H. M. Hutton and T. Schaefer, *Can. J. Chem.*, **40**, 875 (1962).

(6) J. D. Graham and M. T. Rogers, *J. Am. Chem. Soc.*, **84**, 2249 (1962).

(7) J. D. Roberts, "An Introduction to the Analysis of Spin-Spin Splitting in Nuclear Magnetic Resonance," W. A. Benjamin, Inc., New York, 1961.

(8) J. A. Pople, W. G. Schneider and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Company, Inc., New York, 1959.

(9) K. B. Wiberg and B. J. Nist, "The Interpretation of NMR Spectra," W. A. Benjamin, Inc., New York, 1962.

(10) J. D. Swalen and C. A. Reilly, *J. Chem. Phys.*, **37**, 21 (1962).

programs were used to obtain the best agreement between the observed and the calculated spectra. The AB cyclopropyl proton patterns in the n. m. r. spectra of tetrasubstituted cyclopropanes yielded the cyclopropyl coupling directly. The *trans*-cyclopropyl couplings in the ABX type spectra of *trans*-3-(*trans*-2'-carboxypropenyl)-2, 2-dimethylcyclopropane-1-carboxylic acid and its dimethyl ester were determined directly from the AB portion of the spectrum, the downfield part of which was split by the adjacent vinyl hydrogen. The n. m. r. spectra of neat samples of 1, 1-dimethylcyclopropanecarboxylic acid, dimethyl 1-methylcyclopropane-*cis*-1, 2-dicarboxylate and dimethyl 1-methylcyclopropane-*trans*-1, 2-dicarboxylate were analyzed as ABC systems. Identification in the observed spectrum of the three quartets and repeated spacings between lines gave approximate values of the chemical shifts and coupling constants, respectively. Best calculated frequency fits for the four possible combinations of relative signs of couplings were then obtained using the Swalen program.[10] The best fit between observed and calculated intensities was found for the assignments with geminal coupling having an opposite sign to the vicinal couplings in the three ABC systems studied. The analysis of the n. m. r. spectrum of dimethyl 1-methylcyclopropane-*trans*-1, 2-dicarboxylate in benzene gave magnitudes and signs of couplings in agreement with the *neat* compound.

The ^{13}C satellite n. m. r. spectra of 1, 1-dichlorocyclopropane, 1, 1-dimethylcyclopropane, spiropentane and spirohexane were analyzed as AA'XX' systems. The center of each multiplet of the ^{13}C satellites was determined by the moment method.[11] Similar calculated spectra in

---

(11) W. Anderson and H. M. McConnell, *J. Chem. Phys.*, **26**, 1496 (1957).

agreement with the observed spectrum were found for the geminal coupling having either the same or opposite sign to the vicinal couplings. The geminal couplings were assigned opposite signs to the vicinal couplings in these AA'XX' systems on the basis of evidence for the ABC and AA'BB' type proton spectra of substituted cyclopropanes. The _cis_ and _trans_ couplings which have the same signs, are interchangeable without affecting the spectrum. The errors involved in the determination of coupling constants are large due to a high signal-to-noise ratio in the observed spectrum, and also because small changes in the geminal coupling do not have much effect on the calculated spectrum.

The AA'BB' type proton n. m. r. spectrum of neat 1-phenyl-1-bromocyclopropane was solved with the aid of the Swalen program. The only satisfactory fit was obtained with the geminal coupling taken to have the opposite sign to the vicinal couplings. Interchange of the two _cis_ couplings and interchange of the _geminal_ and _trans_ couplings does not affect the calculated spectrum. The assignment of _geminal_ and _trans_ couplings with opposite signs appears to be definite and is supported by analysis of the spectrum of 1-phenyl-1-bromocyclopropane in chloroform (where the chemical shifts are different).

Gutowsky and co-workers[12] on the basis of valence-bond calculations have predicted a positive geminal coupling for H-C-H angles less than 120°. However, a recent publication[13] on the proton n. m. r.

---

(12) H. S. Gutowsky, M. Karplus and D. M. Grant, _J. Chem. Phys._, **31**, 1278 (1959).

spectra of small-ring compounds, indicates that the geminal coupling has an opposite sign to the vicinal couplings in cyclobutane derivatives. With the aid of spin decoupling, Anet[14] has shown that the geminal proton-proton coupling in CHD_2OH is opposite in sign to the ^{13}C-H coupling. Since the latter coupling is almost sure to be positive,[15] the geminal coupling must have a negative sign. On the basis of this evidence we have assigned the geminal coupling a negative sign and the *cis* and *trans* vicinal couplings positive signs in cyclopropanes. It is very interesting that in ethylene oxides, the coupling constants have been reported to have the same relative sign.[16]

The geminal H-C-H angles in cyclopropanes appear to fall in the vicinity of 114.5 -118°[17] and, for this range of angles, the

---

(13) E. Lustig, *J. Chem. Phys.*, **37**, 2725 (1962).

(14) F. A. L. Anet, *J. Am. Chem. Soc.*, **84**, 3767 (1962).

(15) M. Karplus, *J. Am. Chem. Soc.*, **84**, 2458 (1962).

(16) C. A. Reilly and J. D. Swalen, *J. Chem. Phys.*, **32**, 1378 (1960); C. A. Reilly and J. D. Swalen, *J. Chem. Phys.*, **35**, 1522 (1961).

(17) E. Goldish, *J. Chem. Ed.*, **36**, 408 (1959).

theoretical valence-bond curve of Gutowsky and co-workers[12] predicts H-C-H spin-spin couplings of +4.5 to +7 cps. We have investigated the coupling constants in a number of cyclopropanes with different kinds of substituent groups and find the geminal coupling constants between -3.1 to -5.9 cps (Table I). These results contrast with those of Weitkamp and co-workers[18] who report geminal couplings of 7.0 to 9.0 cps for substituted 1,1-dichlorocyclopropanes. In monosubstituted epoxides, the geminal coupling constants have been reported[16] to fall in a narrow range of +5.0 to +6.3 cps for the compounds studied. In ethylene oxides, the H-C-H angle is around 116° and similar geminal couplings in cyclopropanes and ethylene oxides would be expected due to the dependence of the coupling on H-C-H angle. The valence-bond calculations of Karplus[19] and the molecular-orbital treatment of Conroy[20] predict for sp^3 hybridization, a dependence of the vicinal coupling constant on the dihedral angle between the C-H bonds. For the geminal H-C-H angles of 114.5 -118° for cyclopropanes[17] the corresponding dihedral angles are calculated to be 131 -134° for *trans* cyclopropyl hydrogens and 0° for *cis* cyclopropyl hydrogens. The Karplus

---

(18) H. Weitkamp, U. Hasserodt and F. Korte, *Chem. Ber.*, **95**, 2280 (1962).

(19) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

(20) H. Conroy, Advances in Organic Chemistry, Vol. 2, Interscience Publishers, Inc., New York, 1960.

equations predict for these dihedral angles, a *cis* coupling of +8.2 cps and a *trans* coupling of +3.8 to +4.3 cps, while the Conroy curve predicts *cis* and *trans* couplings of +8.0 cps and +6.4 to +7.0 cps, respectively. The vicinal cyclopropyl coupling constants (Table I) are found to be +8.0 to +11.2 cps for *cis* hydrogens and +5.2 to +8.0 for *trans* hydrogens in cyclopropanes. The *cis* coupling was found to be greater than *trans* in cyclopropanes in agreement with theory. In monosubstituted ethylene oxides,[16] the *cis* and *trans* couplings have smaller magnitudes than in cyclopropanes being +4.0 to +5.2 cps and +1.86 to +2.51 cps for *cis* and *trans* protons. The *cis* hydrogens in both cyclopropanes and ethylene oxides are eclipsed and the difference in couplings cannot be accounted for on the basis of dihedral angle. The differences in vicinal couplings may be due to the electronegativity of oxygen in the oxides. Lynden-Bell and Sheppard[21] have analyzed the proton n.m.r. spectra of ^{13}C-labeled acetylene, ethylene and ethane and found the ^{13}C-H coupling to be 249, 156.3 and 125 cps respectively. The fact that the ^{13}C-H values for cyclopropanes (Table I) fall between 157.8 and 166.5 cps reinforces the suggestion[22] that the hybridization of the carbon bonding orbitals in cyclopropanes is close to sp^2. The ^{13}C-H couplings in

---

(21) R. Lynden-Bell and N. Sheppard, *Proc. Roy. Soc.* (London), **A269**, 385 (1962).

(22) N. Muller and D. E. Pritchard, *J. Chem. Phys.*, **31**, 768 (1959).

cyclopropanes may be compared with those observed for allenes[23] which are in the range 166-168 cps and with those for three-membered heterocycles[24] which are in the range 168-176 cps. The ^{13}C-F coupling in octafluorocyclobutane[25] is 298.0 cps. We find for the ^{19}F spectrum of hexafluorocyclopropane a ^{13}C-F coupling of 328.7 cps and a 6.4 cps upfield ^{13}C isotope effect on the fluorine line positions. Not enough data is available to use the magnitude of ^{13}C-F coupling in fluorocyclopropanes to indicate the hybridization of the carbon-bonding orbitals.

A study of chemical shifts in cyclopropanes offers the possibility of giving new insight into the electronic structure of the cyclopropane ring. A large body of evidence has accumulated which supports the concept that the cyclopropane ring system possesses double-bond character.[26] The evidence is based on measurements of dipole moments, ultraviolet and infrared spectra, and ionization potentials as well as on chemical reactivity. Cyclopropane has been suggested

---

(23) E. B. Whipple, J. H. Goldstein and W. E. Stewart, *J. Am. Chem. Soc.*, **81**, 4761 (1959); E. I. Snyder and J. D. Roberts, *J. Am. Chem. Soc.*, **84**, 1582 (1962).

(24) F. S. Mortimer, *J. Mol. Spect.*, **5**, 199 (1962).

(25) R. K. Harris, *J. Phys. Chem.*, **66**, 768 (1962).

(26) See, for example, E. Vogel, *Angew. Chem.*, **72**, 4 (1960).

by Walsh[27] to have bonding corresponding to a three-centered ethylene--the C-C bonds being formed by overlap in the plane of the ring of p orbitals on neighboring carbon atoms and by overlap of three sp^2 orbitals on adjacent carbon atoms directed towards the center of the ring (Figure 1). The Walsh model assumes that two electrons occupy the central hybrid orbitals while four electrons occupy the molecular orbitals formed by overlap of the p-atomic orbitals. Some localized bond character was predicted for cyclopropane leading to hybridization between sp^3 and sp^2 but closer to sp^2. On the basis of a pure valence-state model with perfect pairing, Coulson and Moffitt[28] formulate the carbon-carbon bonds of cyclopropane to involve hybrid orbitals which lie outside the internuclear angles. It was shown that the most favorable hybridization angle corresponds to having the C-C bond-forming orbitals at an angle of 104° which make the difference between internuclear lines and the hybrid orbitals be 22° (Figure 1). The Coulson-Moffitt model predicts the C-H bond orbitals in cyclopropane to have less p-character than normal tetrahedral bonds and hence be more like ethylene than ethane.

Despite the fact that the theoretical models indicate that the C-H bonds in cyclopropane should be more closely akin to those of ethylene than those of ethane, the cyclopropyl resonances come very

---

(27) A. D. Walsh, Trans. Faraday Soc., **45**, 179 (1949).

(28) C. A. Coulson and W. E. Moffitt, Phil. Mag., **40**, 1 (1949).

significantly upfield from the vinyl resonances. Clearly some factor(s) other than carbon hybridization determine the chemical shifts of cyclopropyl hydrogens. Comparison of the cyclopropyl chemical shifts for 1,1-dimethylcyclopropane, spiropentane and spirohexane indicate that as the external C-C-C bond angle is decreased the cyclopropyl resonances are shifted to lower field. (see Table I).

The contribution of magnetic anisotropy[29] of the C-C bonds in cyclopropanes to the proton shielding has been calculated by Wiberg and Nist[30] to be 15 cps. The greater mobility of the carbon electrons in cyclopropane predicted on the basis of the theoretical models compared to ordinary saturated compounds suggests that part of this anomalous diamagnetic shift may be due to a cyclopropane ring-current effect. This could either oppose or reinforce the field of the magnet depending on the position of the attached hydrogen atom relative to the ring. Johnson and Bovey[31] have calculated the chemical shift changes in aromatic systems due to ring current effects by considering the circular precession of the π electrons in two regions above and below the plane of the aromatic ring under the influence of the component of the applied field which is perpendicular to this plane.

---

(29) H. M. McConnell, J. Chem. Phys., 27, 226 (1957).

(30) K. B. Wiberg and B. J. Nist, J. Am. Chem. Soc., 83, 1226 (1961).

(31) C. E. Johnson, Jr., and F. A. Bovey, J. Chem. Phys., 29, 1012 (1958).

The Johnson and Bovey method[31] was applied to the calculation of expected chemical shifts for ring and side-chain hydrogens in several cyclopropanes. The mobile electrons, four for the Walsh model and six for the Coulson and Moffitt model, were assumed to precess in the plane of the cyclopropane ring. Molecular parameters given by Goldish[17] were used. Calculations were carried out for (Case A) the radius of the ring current equal to that of the circle circumscribing the ring (0.88 Å for cyclopropane) and (Case B) of a circle passing through the center of maximum electron density (assumed to 0.5 Å from the carbon atom) of a p orbital oriented as in the Walsh model (1.01 Å for cyclopropane). The results are summarized in Table II and compared with observed shifts.

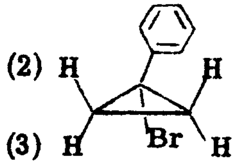
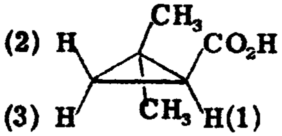
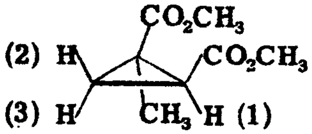
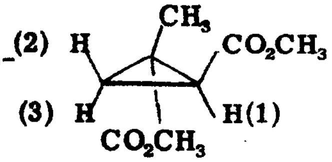
The calculated values are in no more than qualitative agreement with the observed chemical-shift differences. Since some degree of localization of the C-C bond electrons in cyclopropane is likely, the calculated influence of ring currents probably represents upper limits of such effects. It is to be expected that the C-C and C-H bond anisotropies also make substantial contributions to the observed chemical shifts. The assumed ring-current for cyclopropane suggests that a hydrogen located near the equatorial plane of the ring will experience a paramagnetic effect on its resonance position and a diamagnetic effect is predicted for hydrogens inside the ring, or somewhere above it and reasonably close to its three-fold axis. The comparison between experiment and theory shown in Table II cannot be taken as establishing the existence of ring current in cyclopropanes, but the trends are reasonably consistent with a ring-current effect which has also been invoked to explain the unusually large molar diamagnetic susceptibility of cyclopropane.[32]

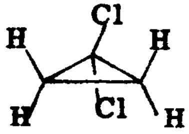
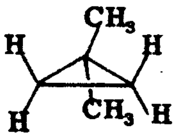
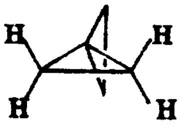
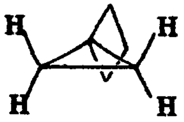
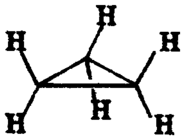
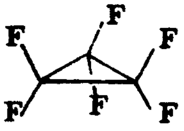
---

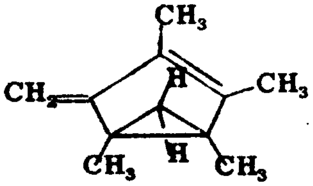
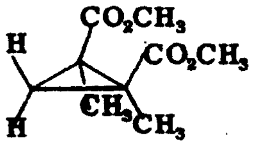
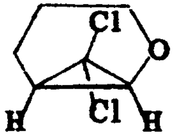
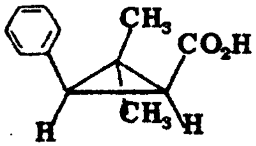
[32] J. R. Lacher, J. W. Pollock and J. D. Park, J. Chem. Phys., 20, 1047 (1952).

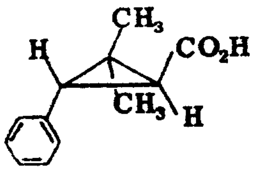
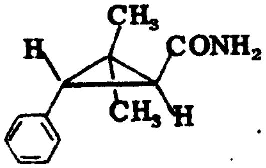
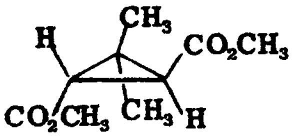
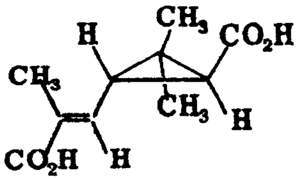
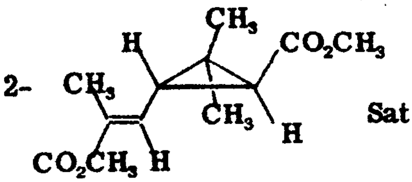
TABLE I

COUPLING CONSTANTS AND CHEMICAL SHIFTS IN CYCLOPROPANE DERIVATIVES

			Coupling Constants cps			Chemical Shifts cps[k]		
Compound	Formula	Solvent	$\underline{J}_{gem}$	$\underline{J}_{cis}$	$\underline{J}_{trans}$	H(1)	H(2)	H(3)
1-Phenyl-1-bromo-cyclopropane		Neat[b]	-5. 9±0. 2	+10. 5±0. 3	+7. 0±0. 2	--	53. 1[a]	70. 1[a]
1, 1-Dimethylcyclo-propanecarboxylic acid		Neat	-4. 3±0. 3	+8. 0±0. 3	+5. 6±0. 3	83. 4	59. 4	47. 5
Dimethyl 1-methyl-cyclopropane-<u>cis</u>-1, 2-dicarboxylate		Neat	-4.7±0. 2	+8. 6±0. 2	+6. 3±0. 2	115. 4	98. 9	69. 1
Dimethyl 1-methyl-cyclopropane-<u>trans</u>-1, 2-dicarboxylate		Neat[c]	-4. 2±0. 2	+8. 8±0. 2	+6. 6±0. 2	133. 4	72. 1	88. 8

Compound	Formula	Solvent	J_{gem}	J_{cis}	J_{trans}	$J_{^{13}CH}$	shift cps^{h}
			Coupling Constants cps				
1, 1-Dichlorocyclopropane		Benzene	-4. 5±1, 0^{d} (+1. 5±1. 0)	+11. 2±0. 5	+8. 0±0. 5	166. 5	88. 2
1, 1-Dimethylcyclopropane		Benzene	-4. 5±1. 0^{d} (+2. 6±1. 0)	+9. 2±0. 5	+5. 4±0. 5	158. 7	12. 0
Spiropentane		Benzene	-3. 9±1. 0^{d} (+2. 4±1. 0)	+8. 9±0. 5	+5. 2±0. 5	159. 8^{e}	43. 8
Spirohexane		Benzene	-5. 1±2. 0^{d} (+2. 3±2. 0)	+9. 7±0. 5	+6. 3±0. 5	157. 8	20. 4
Cyclopropane		5% w/v in CCl_4				161. 8^{f}	13. 2
Hexafluorocyclopropane		$CFCl_3$				$J_{^{13}CF}$ 328. 7	8976±122^{g}

			Coupling Constants cps		
Compound	Formula	Solvent	J_{gem}	J_{cis}	J_{trans}
1, 3, 4, 5-Tetramethyl-2-methylene-bicyclo-[3. 1. 0]hex-3-ene		**Neat**	**(-) 3. 1 ± 0. 2**^{d}		
Dimethyl-1, 2-dimethyl-cyclopropane-<u>cis</u>-1, 2-dicarboxylate		**Neat**	**(-)4. 2 ±0. 2**^{d}		
2-Oxa-7, 7-dichloro-norcarane		**5% w/v in CCl_4**		**(+)8. 6±0. 2**	
2, 2-Dimethyl-<u>cis</u>-3-phenylcyclopropane-1-carboxylic acid		**sat. in $CHCl_3$**		**(+)9. 1±0. 2**	

Compound	Formula	Solvent	Coupling Constants		
			J_{gem}	J_{cis}	J_{trans}
2, 2-Dimethyl-trans-3-phenylcyclopropane-1-carboxylic acid		Sat. in $CHCl_3$			(+)5. 7±0. 2[i]
2, 2-Dimethyl-trans-3-phenylcyclopropane-1-carboxamide		Sat. in $CHCl_3$			(+)6. 0±0. 2[i]
Dimethyl 2, 2-dimethylcyclopropane-trans-1, 3-dicarboxylate		5% in CCl_4			(+)5. 6±0. 2[i, j]
trans-3-(trans-2'-carboxypropenyl)-2, 2-dimethylcyclopropane-1-carboxylic acid		Sat. in $CHCl_3$			(+)5. 7±0. 2[i]
Methyl-trans-3-(trans-2'-carboxypropenyl)-2, 2-dimethylcyclopropane-1-carboxylate		Sat. in $CHCl_3$			(+)5. 4±0. 2[i]

[a] Assigned on the basis that the phenyl group in phenylcyclopropane deshields the *trans* protons more than the *cis* protons.

[b] Magnitudes and signs of coupling constants verified with 1-phenyl-1-bromocyclopropane in chloroform solution.

[c] Magnitudes and signs of coupling constants verified with dimethyl 1-methylcyclopropane-*trans*-1, 2-dicarboxylate in benzene solution.

[d] Sign assumed to be negative.

[e] Taken as twice the frequency difference between the parent peak and the center of the upfield satellite.

[f] In good agreement with the value of 161 cps reported in Ref. 22.

[g] At 56. 4 Mc. relative to fluorotrichloromethane.

[h] Chemical shift in cps from tetramethylsilane for 5% w/v solutions in carbon tetrachloride.

[i] Sign assumed to be positive.

[j] Obtained from ^{13}C satellite spectrum.

[k] Chemical shift in cps from tetramethylsilane

TABLE II

SUMMARY OF CALCULATIONS OF RING CURRENT EFFECTS ON CHEMICAL SHIFTS IN CYCLOPROPANES[a]

Compound	Side-chain, Δ cps					Cyclopropyl, Δ cps				
	Obsvd.	Case A		Case B		Obsvd.	Case A		Case B	
		4e	6e	4e	6e		4e	6e	4e	6e
Cyclopropane						73.2[b]	19.8	29.4	40.8	61.8
Nortricyclene (CH)	18.0[c]	23.4	34.2	29.4	43.8					
1, 1-Dimethylcyclopropane[g]	-9.0[d]	12.6	18.6							
Dicyclopropylmethane[h]	9.6[d]	25.2	37.8							
Spirohexane (in-plane)[e]	-6.0	-8.4	-12.6	-11.4	-17.4					
Spirohexane (out-of-plane)[e]	-6.0	3.6	6.0	6.0	9.6					
Spiropentane[f]						-30.6	-3.6	-6.0	-3.6	-5.4

[a] A positive value of Δ cps indicates an upfield shift while a -Δ cps indicates a downfield shift due to ring-current effect.

[b] Compared with cyclohexane.

[c] Bicyclo[2.2.1]heptane was taken as a model compound in which the cyclopropyl ring was absent.

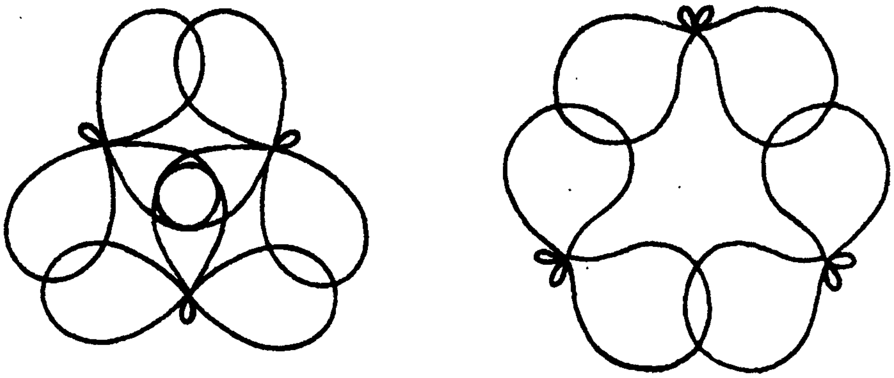
[d] Obtained by comparison with shifts in aliphatic hydrocarbons.

[e] Cyclobutyl hydrogens coplanar or out-of-plane with the cyclopropyl ring; observed Δ cps are relative to cyclobutane.

[f] Calculated Δ cps takes account of modification of ring-current due to a geometry different from cyclopropane.

[g] Calculated as the average for four conformations of the C-H bond.

[h] Assumed to be twice that for 1, 1-dimethylcyclopropane.



Walsh

Coulson and Moffitt

Fig. 1. - Walsh and Coulson and Moffitt orbital models for C-C bonding in cyclopropane rings.

Experimental

The 60-Mc proton n. m. r. spectra of the AB system and ABC, AA'XX', and AA'BB' systems were taken on the V-4300B and A-60 high resolution spectrometers, respectively. The chemical shifts on the V-4300B were measured by means of a Hewlett-Packard Model 200AB audio oscillator and Model 521C frequency counter. Line positions have been measured to an accuracy of 0. 1 cps. Tetramethylsilane was used as an internal reference in the study of AB systems and as an external reference for other systems. Proton and fluorine ^{13}C satellite n. m. r. spectra were taken for ^{13}C in natural abundance. ^{13}C-H coupling constants were obtained as the difference between the chemical shifts of the centers of the low- and high-field satellites.

Hexafluorocyclopropane was a sample generously supplied by Dr. D. C. England of the DuPont Company. The positions of the ^{13}C-satellite peaks were determined at 56. 4 Mc, using side bands from the parent difluoromethylene peak. The chemical shift of the latter peak was measured by interpolation with a 50% solution of hexafluorocyclopropane in fluorotrichloromethane, by generating an approximately 600-cps side band and sweeping rapidly through to the fluorotrichloromethane peak.

1, 1-Dichlorocyclopropane was obtained by photochlorination of cyclopropane. It was distilled through a center-rod fractionating column and the fraction b. p. 74. 5° (744. 5 mm), $n^{25}D$ 1. 4373 (lit.[33] b. p. 74 -75°, $n^{20}D$ 1. 4400) was used.

---

(33) J. D. Roberts and P. H. Dirstine, *J. Am. Chem. Soc.*, **67**, 1281 (1945)

1,1-Dimethylcyclopropane was prepared by Cox[34] and was used without further purification.

Spiropentane of b.p. 36-38° was obtained from Professor D. E. Applequist. It had been distilled after treatment with bromine and dried over calcium hydride.

Spirohexane was furnished by Professor D. E. McGreer.[35]

1-Phenyl-1-bromocyclopropane was prepared in these laboratories by Dr. D. I. Schuster.

Dimethyl 1-Methylcyclopropane-*cis*-1, 2-dicarboxylate. - The parent diacid, m.p. 139-141°, was provided by Professor L. L. McCoy,[36] and was esterified with an excess of diazomethane in benzene. The product was microdistilled at 3 mm. with a bath at 80°.

Dimethyl 1-Methylcyclopropane-*trans*-1, 2-dicarboxylate. - The parent diacid, m.p. *ca.* 170° from Professor L. L. McCoy, was esterified with excess diazomethane. The resulting dimethyl ester was microdistilled at 2 mm. with a bath at 65-70°.

Nortricyclene was a pure sample obtained from Professor H. Hart. The spectrum showed a small broad CH peak, large CH_2

---

(34) E. F. Cox, Ph. D. Thesis, California Institute of Technology, 1955.

(35) D. E. McGreer, *Can. J. Chem.*, **38**, 1638 (1960).

(36) L. L. McCoy, *J. Am. Chem. Soc.*, **80**, 6568 (1958).

peak and a cyclopropyl peak at 114. 6, 70. 8 and 57. 60 cps respectively with areas 1:6:3. The chemical shift for the cyclopropyl peak was measured by side-band superposition from tetramethylsilane, and that for the CH$_2$ and CH peaks by interpolation from two tetramethylsilane side bands. Since the chemical shifts were critical, they were obtained from the maxima or geometric center of each resonance for volume fractions of nortricyclene in carbon tetrachloride of approximately 1, 0. 25, 0. 06, 0. 016 and extrapolating to infinite dilution.

1, 3, 4, 5-Tetramethyl-2-methylene-bicyclo[3. 1. 0]hex-3-ene was obtained from Dr. L. deVries.[37] Two side bands from the vinyl peak were used to obtain the frequencies of the cyclopropyl peaks by interpolation, the chemical shift difference between the cyclopropyl hydrogens being 3. 9 cps. The chemical shift of the center of the cyclopropyl methylene quartet was measured by interpolation from side bands from tetramethylsilane for a 5% w/v solution of the hydrocarbon in carbon tetrachloride and found to be 31. 2 cps.

2-Oxa-7, 7-dichloronorcarane of b. p. 50-52° (1. 6-1. 9 mm.) $n^{25.7}_{D}$ 1. 4981 was provided by Professor W. E. Parham.[38] The n. m. r. spectrum of a 5% w/v solution of 2-oxa-7, 7-dichloronorcarane in carbon tetrachloride showed two main groups of peaks, the larger group at high-field being assigned to the methylene hydrogens at C4, C5 and the cyclo-

---

(37) L. deVries, *J. Am. Chem. Soc.*, **82**, 5242 (1960).

(38) E. E. Schweizer and W. E. Parham, *J. Am. Chem. Soc.*, **82**, 4085 (1960).

propyl methine hydrogen at C6; and the smaller group at low-field to the methylene hydrogens at C3 and the cyclopropyl methine hydrogen at C1. The latter gave a prominent unsymmetrical doublet on the low-field side of the lower group of peaks, due to *cis*-vicinal spin coupling with the cyclopropyl methine hydrogen at C6. The frequencies of the peaks in this doublet were determined by side-band superposition from tetramethylsilane.

Dicyclopropylmethane was provided by Professor H. Hart.[39] The acyclic methylene resonance appeared as a broadened doublet near the cyclopropyl methine peaks. The chemical shift for the center of this doublet was obtained by extrapolation to infinite dilution and found to be 65.4 cps downfield from tetramethylsilane.

***trans*-3-(*trans*-2'-Carboxypropenyl)-2,2-dimethylcyclopropane-1-carboxylic acid** was the dextrorotatory enantiomer, m.p. 164-165°, obtained from Professor Y. Inouye.[40] The line positions were measured by superimposing side bands from chloroform.

Methyl *trans*-3-(*trans*-2'-carbomethoxypropenyl)-2,2-dimethylcyclopropane-1-carboxylate, m.p. 80° was also provided by Professor Y. Inouye.

---

(39) H. Hart and O. E. Curtis, *J. Am. Chem. Soc.*, **78**, 112 (1956).

(40) Y. Inouye, *Bull. Inst. Chem. Res., Kyoto Univ.*, **35**, 49 (1957); *C. A.*, **52**, 11759 (1958).

2, 2-Dimethyl-*trans*-3-phenylcyclopropane-1-carboxylic acid was provided by Professor F. Sorm[41] and had m.p. 102°. Approximate chemical shifts (accurate to ± 1 cps) were obtained for the methyl and cyclopropyl hydrogens by interpolation from a tetramethylsilane peak (internal reference) and the low-field cyclopropyl doublet, which has been accurately calibrated. The chemical shift differences were thus found to be 48 cps between the cyclopropyl hydrogens and 31 cps between the gem dimethyl groups.

2, 2-Dimethyl-cis-3-phenylcyclopropane-1-carboxylic acid was also provided by Professor Sorm and had m.p. 134°. The chemical shift between the cyclopropyl hydrogens was 39 cps, and between the *gem* dimethyl groups only 2 cps.

2, 2-Dimethyl-*trans*-3-phenylcyclopropane-1-carboxamide was obtained from Professor G. W. Perold.[42] The chemical shifts were approximately 55 cps between the cyclopropyl hydrogens and 27 cps between the *gem* dimethyl groups.

Dimethyl 2, 2-dimethylcyclopropane-*trans*-1, 2-dicarboxylate-- The parent diacid was obtained from Professors Y. Inouye and M. Matsui, who report m.p. 210-212° and 212-213° respectively. The combined samples were esterified with excess diazomethane, and the product was

---

[41] J. Karkas, P. Kourim and F. Sorm, *Chem. listy*, **52**, 695 (1958); *C. A.*, **52**, 13651 (1958).

[42] G. W. Perold, *J. S. African Chem. Inst.*, **10**, 11 (1957).

microdistilled at 14 mm. with a bath at 125-130° and gave diester of $\underline{n}^{24}\underline{D}$ 1.4434. The high-field cyclopropyl ^{13}C satellite was a slightly unsymmetrical doublet. The resonances were calibrated by side-band superposition from the carbomethoxyl peak.

Dimethyl 1, 2-dimethylcyclopropane-cis-1, 2-dicarboxylate was provided by Professor L. L. McCoy and contained 7% of the *trans* isomer. Two side bands from the methyl peaks were placed on either side of the upfield cyclopropane doublet and the splitting determined by interpolation. The analysis of the cyclopropyl methylene quartet indicated that the chemical shift between the cyclopropyl hydrogens was 79.0 cps.

Acknowledgement. - Besides the generous gifts of samples of cyclopropane derivatives mentioned above, we are deeply grateful to Drs. A. A. Bothner-By, J. D. Swalen and Professor K. B. Wiberg for supplying us with program decks for the calculation and fitting of n. m. r. spectra for use with the IBM 7090 computer. Mr. K. Servis and Mr. L. Sloan provided extensive help with the computations.

TECHNICAL REPORT DISTRIBUTION LIST

CONTRACTOR CALIFORNIA INSTITUTE OF TECHNOLOGY NR NO. 055-388

CONTRACT NUMBER Nonr 220(26) DATE 16 FEB 1962

	NO. COPIES
Commanding Officer Office of Naval Research Branch Office The John Crerar Library Building 86 East Randolph Street Chicago 1, Illinois	(1)
Commanding Officer Office of Naval Research Branch Office 346 Broadway New York 13, New York	(1)
Commanding Officer Office of Naval Research Branch Office 1030 East Green Street Pasadena 1, California	(1)
Commanding Officer Office of Naval Research Branch Office Box 39 Navy #100 Fleet Post Office New York, New York	(7)
Director, Naval Research Laboratory Washington 25, D. C. Attn: Technical Information Officer Chemistry Division	(6) (2)
Chief of Naval Research Department of the Navy Washington 25, D. C. Attn: Code 425	(2)
DDR&E Technical Library Room 3C-128, The Pentagon Washington 25, D. C.	(1)
Technical Director Research & Engineering Division Office of the Quartermaster General Department of the Army Washington 25, D. C.	(1)
Research Director Clothing & Organic Materials Division Quartermaster Research & Engineering Command U. S. Army Natick, Massachusetts	(1)
Air Force Office of Scientific Research (SRC-E) Washington 25, D. C.	(1)
Commanding Officer Diamond Ordnance Fuze Laboratories Washington 25, D. C. Attn: Technical Information Office Branch 012	(1)
Office, Chief of Research & Development Department of the Army Washington 25, D. C. Attn: Physical Sciences Division	(1)
Chief, Bureau of Ships Department of the Navy Washington 25, D. C. Attn: Code 342C	(2)
Chief, Bureau of Naval Weapons Department of the Navy Washington 25, D. C. Attn: Technical Library	(4)
ASTIA Document Service Center Arlington Hall Station Arlington 12, Virginia	(10)
Director of Research U.S. Army Signal Research & Development Laboratory Fort Monmouth, New Jersey	(1)
Naval Radiological Defense Laboratory San Francisco 24, California Attn: Technical Library	(1)
Naval Ordnance Test Station China Lake, California Attn: Head, Chemistry Division	(1)

REVISED 1 FEB 1962

TECHNICAL REPORT DISTRIBUTION LIST

Page 2

CONTRACTOR CALIFORNIA INSTITUTE OF TECHNOLOGY

NR NO. 055-388

CONTRACT NUMBER Nonr 220(26)

DATE

NO. COPIES

Commanding Officer
Army Research Office
Box CM, Duke Station
Durham, North Carolina
Attn: Scientific Synthesis Office (1)

Brookhaven National Laboratory
Chemistry Department
Upton, New York (1)

Atomic Energy Commission
Division of Research
Chemistry Programs
Washington 25, D. C. (1)

Atomic Energy Commission
Division of Technical Information Extension
Post Office Box 62
Oak Ridge, Tennessee (1)

U.S. Army Chemical Research and
Development Laboratories
Technical Library
Army Chemical Center, Maryland (1)

Office of Technical Services
Department of Commerce
Washington 25, D. C. (1)

Dr. John E. Leffler
Department of Chemistry
Florida State University
Tallahassee, Florida (1)

Dr. R. W. Taft, Jr.
Department of Chemistry
Pennsylvania State University
University Park, Pa. (1)

ONR Branch Office
495 Summer Street
Boston 10, Mass.
Attn: Dr. A. L. Powell (1)

NO. COPIES

Dr. G. Barth-Wehrenalp, Director
Inorganic Research Department
Pennsalt Chemicals Corporation
P. O. Box 4388
Philadelphia 18, Pennsylvania (2)

Dr. M. S. Newman
Department of Chemistry
Ohio State University
Columbus, Ohio (1)

Dr. P. Bartlett
Department of Chemistry
Harvard University
Cambridge, Mass. (1)

Dr. S. Winstein
Department of Chemistry
University of California
Los Angeles 24, Calif. (1)

Dr. L. P. Hammett
Department of Chemistry
Columbia University
New York 27, N. Y. (1)

Dr. H. C. Brown
Department of Chemistry
Purdue University
Lafayette, Indiana (1)

Dr. H. S. Gutowsky
Department of Chemistry
University of Illinois
Urbana, Illinois (1)

Dr. D. A. Brown
Department of Chemistry
University College
Upper Merrion Street
Dublin, Ireland (1)

Dr. T. L. Heying
Organics Division
Olin Mathieson Chemical Corporation
275 Winchester Avenue
New Haven, Conn. (1)

TECHNICAL REPORT DISTRIBUTION LIST

Page

CONTRACTOR CALIFORNIA INSTITUTE OF TECHNOLOGY
NR NO. 055-388

CONTRACT NUMBER Nonr 220(26)
DATE

	NO. COPIES		NO. COPIES
Monsanto Research Corporation Everett Station Boston 49, Mass. Attn: Mr. K. Warren Easley	(1)		
Dr. M. S. Cohen, Chief Propellants Synthesis Section Reaction Motors Division Denville, New Jersey	(1)		
Dr. M. J. S. Dewar Department of Chemistry University of Chicago Chicago 37, Illinois	(1)		
Dr. T. P. Onak Department of Chemistry Los Angeles State College Los Angeles, Calif.	(1)		
Dr. Riley Schaeffer Department of Chemistry Indiana University Bloomington, Indiana	(1)		
Dr. W. N. Lipscomb Department of Chemistry Harvard University Cambridge 38, Mass.	(1)		
Naval Research Laboratory Washington 25, D.C. Attn: Dr. R. B. Fox	(1)		
Dr. D. L. Venezky Code 6120 (added 1-7-63)	(1)		
Dr. E. Grunwald Bell Telephone Laboratories Murray Hill, New Jersey (added 1-7-63)	(1)		