($CHCl_3$) 5.82 μ; nmr (CCl_4) δ 1.40 (t, 3 H, J = 7.0 Hz), 4.37 (q, 2 H, J = 7.0 Hz).

Methyl Benzoate.—Treatment of 144 mg of phenyl orthothioformate with 665 mg of mercuric chloride and 213 mg of mercuric oxide in 14 ml of 7.7% aqueous methanol under conditions identical with those above yielded 66 mg (95.5%) of methyl benzoate: ir (CCl_4) 5.78 μ, nmr ($CDCl_3$) δ 3.89 (s, 3 H).

Ethyl Pentanoate.—Treatment of 1.88 g (8.46 mmol) of 2-butyl-1,3-dithiane in 20 ml of tetrahydrofuran with 5.70 ml (12.8 mmol) of *n*-butyllithium followed by 1.72 ml (19.35 mmol) of methyl disulfide in a manner identical with the above procedure yielded 2.13 g (89.8%) of crude orthothioformate derivative as an orange oil: nmr (CCl_4) δ 2.00 (s, 3 H). *Anal.* Calcd: C, 48.60; H, 8.16. Found: C, 49.12; H, 8.15. Crude product (222 mg, 1 mmol) was refluxed for 4 hr in 27 ml of 95% ethanol with 1.14 g of mercuric chloride and 353 mg of mercuric oxide. Work-up as above yielded 132 mg (quantitative) of the ester as a clear, light brown oil: ir ($CHCl_3$) 5.80 μ.

Ethyl Cinnamate.—A solution of 2.38 g (10.68 mmol) of 2-(β-styryl)-1,3-dithiane in 20 ml of tetrahydrofuran was treated with 5.70 ml (12.8 mmol) of *n*-butyllithium and subsequently with 1.73 ml (19.35 mmol) of methyl disulfide as above to give 2.56 g (90%) of the orthothioformate derivative as a clear yellow oil: nmr ($CDCl_3$) δ 2.04 (s, 3 H), 6.30 (d, 1 H, J = 10.0 Hz), 6.90 (d, 1 H, J = 10.0 Hz). *Anal.* Calcd: C, 58.16; H, 6.01. Found: 57.80; H, 5.83. Crude product (268 mg, 1 mmol) was refluxed for 7.5 hr in 95% ethanol with 1.14 g of mercuric chloride and 353 mg of mercuric oxide. The standard work-up yielded 162 mg (92.1%) of oily ethyl cinnamate: nmr (CCl_4) 1.24 (t, 3 H, J = 7.0 Hz), 4.15 (q, 2 H, J = 7.0 Hz), 6.37 (d, 1 H, J = 16.5 Hz), 7.63 (d, 1 H, J = 16.5 Hz); ir (CCl_4) 5.82, 6.10 μ.

Isomerization of 6 to 7.—The cinnamyl orthothioformate was bulb to bulb distilled in a Kugelrohr apparatus at 192° and 50 μ to give an oil. The nmr spectrum ($CDCl_3$) of this material showed peaks corresponding to a small amount of **9** and new resonances at δ 1.98 (s, 3 H), 5.08 (d, 1, H, J = 10.0 Hz), and 6.05 (d, 1 H, J = 10.0 Hz) which were attributed to isomer **10**. Integration of the spectrum showed **9** and **10** to be present in a ratio of 2.6:7.4.

Benzoic Acid.—Phenyl orthothioformate **3** (238 mg, 1 mmol) was refluxed in 27 ml of 35% aqueous acetone with 1.14 g of mercuric chloride and 353 mg of mercuric oxide for 24 hr. The reaction was cooled and worked up in a manner identical with the esterification reaction. The methylene chloride extract was washed with 10% aqueous sodium carbonate. Acidification of the aqueous layer followed by extraction with methylene chloride yielded 80 mg (69%) of benzoic acid which was homogeneous in the nmr spectrum, mp 122°.

Cinnamic Acid.—The cinnamyl orthothioformate (508 mg, 2 mmol) was similarly refluxed in 50 ml of 35% aqueous acetone with 1.63 g of mercuric chloride and 1.30 g of mercuric oxide for 21 hr. Typical work-up yielded 131 mg (46%) of cinnamic acid: mp 133–144°; nmr ($CDCl_3$) δ 6.55 (d, 1 H, J = 16.5 Hz), 7.88 (d, 1 H, J = 16.5 Hz), 10.7 (s, 1 H); ir ($CDCl_3$) 5.93, 6.13 μ.

Pentanoic Acid.—Butyl orthothioformate (224 mg, 1 mmol) was similarly refluxed in 25 ml of 35% aqueous acetone with 823 mg of mercuric chloride and 658 mg of mercuric oxide for 25 hr. Typical work-up yielded 42 mg (40%) of oily pentanoic acid: nmr ($CDCl_3$) δ 9.58 (s, 1 H); ir ($CDCl_3$) 3.05–4.35, 5.85 μ.

Reaction of Phenyl Orthothioformate (3, R = Phenyl) with *tert*-Butyl Alcohol.—A mixture of 142 mg (0.6 mmol) of phenyl orthothioformate, 665 mg of mercuric chloride, and 213 mg of mercuric oxide was refluxed with 12 ml of *tert*-butyl alcohol and 1 ml of water for 67.5 hr. The reaction was cooled and filtered and the residue was washed with methylene chloride. The filtrate was washed with 20% aqueous ammonium chloride and saturated aqueous sodium chloride, dried, and evaporated to yield 62 mg of amorphous solid. This material was dissolved in methylene chloride and extracted with 10% aqueous sodium bicarbonate. Acidification of the aqueous layer followed by methylene chloride extraction yielded 43 mg (60.3%) of benzoic acid, mp 119–120°.

Stability of *tert*-Butyl Benzoate.—*tert*-Butyl benzoate was prepared according to procedure 1 of Raha.[6] *tert*-Butyl benzoate (173 mg, 1 mmol) was dissolved in 24 ml of *tert*-butyl alcohol and 2 ml of distilled water with 1.4 g of mercuric chloride and 430 mg of mercuric oxide. The mixture was refluxed for 72 hr and then worked up as above to give 172 mg of recovered *tert*-butyl benzoate. No additional products were evident in the nmr spectrum.

Orthothioformates *via* 2-Thiomethoxy-1,3-dithiane. Ethyl Pentanoate.—2-Thiomethoxy-1,3-dithiane was prepared from 1,3-dithiane (1.0 g, 8.32 mmol) by treatment with *n*-butyllithium (4.0 ml, 8.8 mmol) followed by methyl disulfide (0.752 ml, 8.5 mmol) in a manner identical with that above. The crude product was isolated as an oil (1.72 g, 92%). To 168 mg (1.01 mmol) of crude thiomethoxy derivative in 5 ml of tetrahydrofuran at −20° was injected 0.5 ml (1.02 mmol) of *n*-butyllithium over a period of 1 min. After 3 min of stirring, 0.114 ml (1.0 mmol) of methyl iodide was added and stirring was continued for 2.5 hr. The reaction was brought to 0° and stored for 17 hr followed by 3 hr at 25°. The reaction was subjected to the usual work-up to yield 175 mg of yellow oil with properties identical with those of the butyl orthothioformate previously described. Treatment of 166 mg of this oil with 95% ethanol under typical alcoholysis conditions yielded crude ethyl pentanoate (94 mg, 97%).

Registry No.—Ethyl benzoate, 93-89-0; 2-thiomethoxy-2-phenyl-1,3-dithiane, 34858-82-7; methyl benzoate, 93-58-3; ethyl pentanoate, 539-82-2; ethyl cinnamate, 4192-77-2; benzoic acid, 65-85-0; cinnamic acid, 621-82-9; pentanoic acid, 109-52-4.

Acknowledgment.—We are grateful to the Graduate School of the University of Wisconsin for financial support of this work and to the National Science Foundation for support to C. C. W. under the auspices of the undergraduate research participation program (GY-8817, 1971).

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[6] C. Raha, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 263.

A Nuclear Magnetic Resonance Technique for Distinguishing Isomers of 3,5-Disubstituted Nortricyclenes[1a]

Boris Franzus,* Stephen Wu,[1b] W. C. Baird, Jr.,[1c] and Monte L. Scheinbaum

Department of Chemistry, East Tennessee State University, Johnson City, Tennessee 36701

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Known techniques for assigning relative stereochemistry to the 3,5 positions of nortricyclene derivatives are generally limited to compounds with a "trans" arrangement of substituent groups as in **1a**.[2-6] Nmr techniques for distinguishing between the "cis" isomers **1b** and **1c** (X = Y) have not been reported.

The symmetry of the parent nortricyclene system includes a threefold axis of rotation through the bridgehead carbon (C_4) and the center of the cyclopropyl ring (C_{3v} symmetry). The same sets of rules employed in the interpretation of spectra of norbornene and norbornadiene systems do not apply to the nortricyclyl system. The terms endo and exo do not have the same significance in considering the nortricyclene system, for which of the three carbons chosen as the

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[1] (a) Presented in part at the Southeast Regional Meeting of the American Chemical Society, Nashville, Tenn., Nov 4–6, 1971; (b) Abstracted in part from the M.S. Thesis of Stephen Wu, East Tennessee State University, Aug 1970; (c) Corporate Research Laboratories, Esso Research and Engineering Company, Linden, N. J.

[2] S. J. Cristol, J. K. Harrington, and M. S. Singer, *J. Amer. Chem. Soc.*, **88**, 1529 (1966).

[3] D. G. Trecker and J. P. Henry, *ibid.*, **85**, 3204 (1963).

[4] R. S. Neale and E. B. Whipple, *ibid.*, **86**, 3130 (1964).

[5] D. R. Coulson, *ibid.*, **91**, 200 (1969).

[6] J. R. Stille and L. F. Hines, *ibid.*, **92**, 1798 (1970).

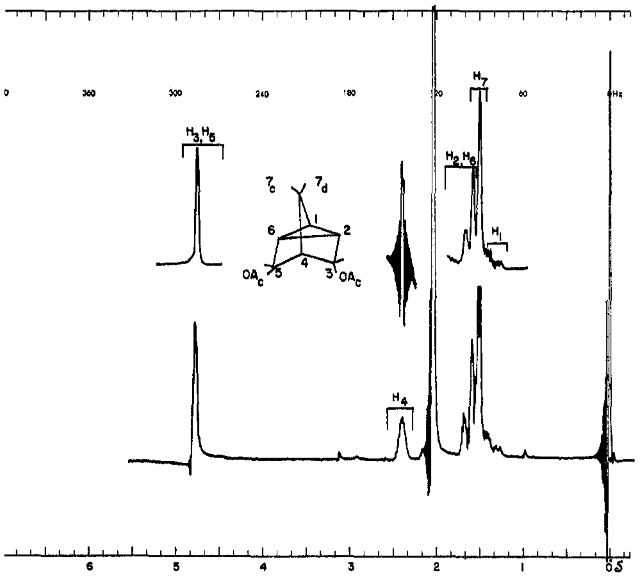
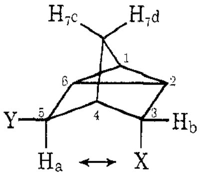
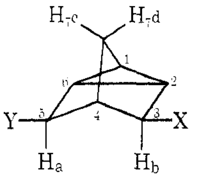


Figure 1.—Nmr spectrum of the 3,5-*endo,endo*-diacetate (**4**). Inset, spectrum of **4** after irradiation of the bridgehead proton H_4.

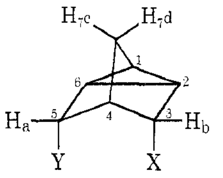
bridge (C_3, C_5, C_7) is arbitrary. Hence, assignments of stereochemistry based on experience with coupling constants in the norbornyl or norbornadienyl derivatives cannot be made in the nortricyclene case. The use of a monosubstituted reference compound to determine chemical shifts of endo or exo protons is meaningless; there are only *R* and *S* isomers of 3-substituted nortricyclenes.



1a



1b

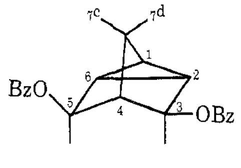


1c

A technique based upon nmr analysis of the high-field spectra has been developed in these laboratories for assigning stereochemistry to cis,exo and cis,endo isomers of 3,5-disubstituted nortricyclenes. This technique depends upon the fact that an *exo-Y substituent at position 5* (*as in* **1a** *or* **1b**) *should cause a paramagnetic shift of* H_{7c}, for, owing to the symmetry of the nortricyclene system, the H_{7c}–Y interaction in **1a** and **1b** is similar to the H_a–X interaction in **1a**. In the same vein, an *endo-X substituent at position 3* (*as in* **1a** *or* **1c**) *would not affect the chemical shift of either* H_{7c} *or* H_{7d}.

Nmr analyses of reported 3,5-disubstituted nortricyclenes of known stereochemistry have been carried out with particular emphases on the high-field portions of the spectra (H_1, H_2, H_6, and H_7). The compounds used in these studies were the 3,5-*exo,exo*- and *endo,endo*-dibenzoate derivatives, **2** and **3** respectively,[7] the 3,5-*endo,endo*-diacetate **4**,[7] and the *exo,exo*-diacetamide **5**.[8]

If indeed the paramagnetic shift is a general phenomenon, then the H_{7c}, H_{7d} protons of the "pseudo" exo,exo isomer (**1b**, X = Y) would appear at lower field (paramagnetic shift) than the H_{7c}, H_{7d} protons of the corresponding "pseudo" endo,endo isomer (**1c**, X = Y). The critical task in these nmr analyses was assignment of H_7 for both the "pseudo" exo,exo and endo,endo isomers. Since H_7 is magnetically coupled to H_4 (and H_1), irradiation of H_4 should sharpen the H_7 signal. Identification of H_4 in each of the spectra presented little problem, since the H_4 signal appeared downfield with respect to the H_1, H_2, H_6, and H_7 absorptions, owing to its bridgehead nature and to its proximity to the electronegative X groups (at C_3 and C_5). In all cases, irradiation of H_4 resulted in sharpening of the downfield protons (H_3, H_5) and sharpening of the bridge protons (H_7). For example, irradiating H_4 of the 3,5-*endo,endo*-diacetate (**4**, X = Y = Ac) resulted in collapse of the signals at δ 1.53 ppm; therefore the absorption at 1.53 ppm can be assigned to H_7 (see Figure 1). The same technique was applied to compounds **2**, **3**, and **5** to ascertain the chemical shift of H_7 in each case. Further proton decoupling and spectral simulation led to chemical shift assignments of the protons in compounds **2**–**5**. These results are shown in Table I.



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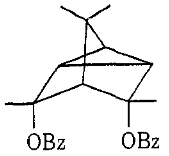

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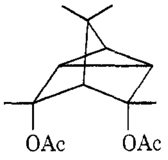

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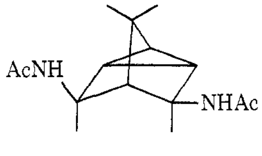

5

Bz ≡ COC_6H_5
Ac ≡ $COCH_3$
(unspecified positions are hydrogens)

Table I

Chemical Shift Assignments

Hydrogen	Chemical shift, δ			
	2	3	4	5
H_1	1.60	1.39	1.44	1.30
H_{7c} = H_{7d}	1.99	1.53	1.53	1.56
H_2 = H_6	1.70	1.71	1.64	1.36
H_4	2.49	2.59	2.44	2.13
H_3 = H_5	4.88	4.96	4.84	3.77

Protons H_7 would be expected to absorb at higher field than H_2, H_6 even though the latter are "cyclopropyl" type hydrogens, since H_7 is one carbon further removed from the electronegative X groups. However, H_7 should absorb at lower field than H_1, for both protons are about equally removed from C_3 and C_5, but H_1 is a "cyclopropyl" type proton. These predictions hold true for the 3,5-di-endo isomers **3** and **4**, wherein H_1 absorbs at higher field than H_7, which in turn absorbs higher than H_2, H_6.

This order of absorption is *not* observed for the 3,5-di-exo compounds **2** and **5**. For compounds **2** and **5**, proton H_1 still absorbs at the highest field, but the

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[7] W. C. Baird, Jr., and M. Buza, *J. Org. Chem.*, **33**, 4105 (1968).

[8] M. L. Scheinbaum, *ibid.*, **35**, 2785 (1970).

TABLE II

COUPLING CONSTANTS OF THE NORTRICYCLIC SYSTEM

	Coupling constant J,[a] Hz			
J	**2**	**3**	**4**	**5**
$J_{1,2} \equiv J_{1,6}$	5.3–5.5[b]	5.3–5.5	5.3–5.5 (5.46)[e]	5.3–5.5[f]
$J_{1,7}$	1.2–1.5	1.2–1.5	1.2–1.5	1.2–1.5
$J_{4,7}$	1.8–2.0	1.8–2.0	1.8–2.0	1.8–2.0
$J_{2,3} \equiv J_{5,6}$	0.5[c]	0.75[d]	0.75	
$J_{3,4} \equiv J_{4,5}$	1.3–1.5	1.3–1.5	1.3–1.5	1.3–1.5
$J_{3,7} \equiv J_{5,7}$	0.0[d]	0.9[d]		
$J_{2,4} \equiv J_{4,6}$		≤ 0.3[c]	≤ 0.3	

[a] It was not possible to obtain signs of coupling constants in this work. [b] This coupling constant was assumed from analogy with compound **3** and was found to fit the spectral simulation. The order of magnitude was also checked by the hand calculation of an AB_2 type spectrum. [c] Estimated from sharpening of peak after irradiation. Such coupling constants are known to be small. See M. Barfield and B. Chakrabati, *Chem. Rev.*, 69, 757 (1969). [d] Estimated from sharpening of peak from triple resonance. [e] Based on coupling constants from endo,endo compounds and the spectral simulation. [f] This was based on a hand calculation of an AB_2 system. See, for example, J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution NMR Spectroscopy," Vol. I, Pergamon Press, New York N. Y., 1965, pp 321–329.

H_2, H_6 signals are at *higher* field than H_7. It is quite clear from Table I that H_7 (in compound **2**) absorbs about 0.3 ppm lower than H_2, H_6; in compound **5**, H_7 absorbs at 0.2 ppm lower than H_2, H_6. These results are completely consistent with previous observations showing that protons spatially adjacent to electron-attracting groups suffer a paramagnetic (downfield) shift.

Additional evidence corroborating the H_{7c}–H_{7d} assignment (δ 1.57 ppm) for the endo,endo isomer **3** and the H_{7c}–H_{7d} assignment (δ 1.99 ppm) for the exo,exo isomer **2** came from observation of the chemical shifts of each of these compounds (**2** and **3**) in the presence of tris(dipivalomethanato)europium, Eu(DPM)$_3$.[9–13] Since the effect of Eu(DPM)$_3$ decreases with distance it was anticipated that all the protons in the 3,5-*exo,exo*-dibenzoate **2** would suffer some paramagnetic shift, for the Eu(DPM)$_3$ should be spatially proximate to all the hydrogens in **2**. In contrast to the exo,exo isomer **2**, the Eu(DPM)$_3$ would be expected to interact with all the protons of the 3,5-*endo,endo*-dibenzoate **3** *except the bridge hydrogens (7c, 7d)*. Addition of Eu(DPM)$_3$ to **2** resulted in a chemical shift of all signals; addition of Eu(DPM)$_3$ to **3** resulted in a sizable chemical shift of all signals *except those for* H_{7c} *and* H_{7d}.

The generality of paramagnetic shifts for various electronegative X groups has been shown for chloride,[3,5] bromide,[2,5] acetate,[4] carbomethoxy,[6] and phenylsulfone groups.[2] This study has extended the above grouping to include benzoates, acetates,[14] and acetamides wherein the groups are identical (X = Y).[15]

In summary, paramagnetic shifts of bridge protons (H_7) in contrast to "cyclopropyl" hydrogens (H_2 and H_6) are observed for 3,5-di-exo compounds, whereas bridge proton absorptions are observed at higher fields than those for "cyclopropyl" hydrogens in 3,5-di-endo derivatives. One can distinguish between 3,5-di-exo and 3,5-di-endo derivatives by irradiation of the bridgehead hydrogen (H_4), thereby revealing the decoupled signals for the bridge protons (H_7). If the bridge hydrogens absorb at lower field than the "cyclopropyl" protons (H_2 and H_6), then the compound is di-exo; if not, it is di-endo.

Experimental Section

Nmr spectra (60 and 100 MHz) were run on a JEOLCO C-60H at East Tennessee State University and on a JNM-4H-100 at Medford, Mass. A JEOLCO-SD-30 was used for homonuclear spin decoupling. Samples for nmr analysis were dissolved in $CDCl_3$ with tetramethylsilane (TMS) as internal standard. Chloroform-*d*, however, was not used as solvent for compound **5**; CD_3CO_2D (99.5% isotopically pure from Diaprep, Inc.) was used as solvent with TMS as internal standard. All compounds were prepared as previously described,[7,8] and had the correct elemental analyses.

Although the chemical shifts and coupling constants assigned in this study do not necessarily form a unique set,[16,17] these parameters have been so chosen that they are consistent with those values found in analogous systems. Values of bridge–bridgehead coupling constants of 1.5–2.5 Hz are consistent with previous studies;[18–21] the 5.5-Hz coupling constants ($J_{1,2} \equiv J_{1,6}$) of "nortricyclic" three-membered ring cis protons are not inconsistent with other literature values.[22–26] These results are summarized in Table II.

Spectral Simulation.—Spectral simulation was done using an (8K) IBM-1130 with plotter and a computer program designed for five spins. Comparison spectra were obtained from both double and triple resonance (homonuclear) experiments. These were compared to the simulated spectra. The 3,5-disubstituted nortricyclyl system has eight protons, but the chemical shift of the 3,5 hydrogens are the same, reducing the number of spins to seven. Decoupling was necessary in order to reduce the number of spins to five for comparison of simulated spectra with actual spectra.

Experiments with Chemical Shift Reagent.—To an nmr tube, containing about 100 mg of 3,5-*exo,exo*-dibenzoate (**2**) and 0.5 ml of $CDCl_3$, about 12 mg of Eu(DPM)$_3$ was introduced. A solution containing about 90 mg of the 3,5-*endo,endo*-dibenzoate (**3**), 0.5 ml of $CDCl_3$, and about 16 mg of Eu(DPM)$_3$ was prepared

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(9) C. C. Hinckley, *J. Amer. Chem. Soc.*, **91**, 5160 (1969).

(10) J. K. M. Sanders and D. H. Williams, *Chem. Commun.*, 422 (1970).

(11) George H. Wahl, Jr., and M. R. Peterson, Jr., *ibid.*, 1167 (1970).

(12) P. V. Demarco, T. K. Elzey, R. Burton Lewis and E. Wenkert, *J. Amer. Chem. Soc.*, **92**, 5734 (1970).

(13) E. Wedejs and M. S. Salomon, *ibid.*, **92**, 6965 (1970).

(14) A sample of the "trans" 3,5-diacetate (**1a**, X = Y = OAc) showed two different downfield signals for H_3 and H_5 with a difference in chemical shift of about 0.3 ppm.

(15) We sympathize with a referee's query as to how many cases are necessary to demonstrate the generality of a phenomenon; we hope that the seven different electronegative groupings that have shown this effect are sufficient to establish the generality of the paramagnetic shift effect.

(16) S. Castellano and J. S. Waugh, *J. Chem. Phys.*, **34**, 295 (1961).

(17) S. Castellano and J. S. Waugh, *ibid.*, **35**, 1900 (1961).

(18) P. Laszlo and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **86**, 1171 (1964).

(19) E. I. Snyder and B. Franzus, *ibid.*, **86**, 1166 (1964).

(20) J. C. Davis, Jr., and T. V. VanAuken, *ibid.*, **87**, 3900 (1965).

(21) B. Franzus, W. C. Baird, Jr., N. F. Chamberlain, T. Hines, and E. I. Snyder, *ibid.*, **90**, 3721 (1968).

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(24) F. A. Bovey, "Nuclear Magnetic Resonance Spectroscopy," Academic Press, New York, N. Y., 1969.

(25) C. A. Reilly and J. Swalen, *J. Chem. Phys.*, **32**, 1378 (1960).

(26) M. S. Gutowsky, M. Karplus, and D. M. Grant, *ibid.*, **31**, 1278 (1959).

in an nmr tube. The paramagnetic shifts undergone by various protons (TMS as internal standard) are shown in Table III.

TABLE III

3,5-*exo,exo*-Dibenzoate (**2**)	3,5-*endo,endo*-Dibenzoate (**3**)	
Hydrogens	Ppm	Ppm
H_1		0
H_2, H_6	0.05	0.12
H_{7c}, H_{7d}	0.07	0
H_4	0.10	0.17
H_3, H_5	0.10	0.27

The chemical shifts and coupling constants obtained in this study were reliable enough to be used for computer simulation of the actual high-field spectra of compounds **3** and **4**. Long-range coupling could not be demonstrated on the simulated spectrum owing to the five-spin computer limitation. However, irradiation of H_4 eliminated the long-range coupling of H_4, resulting in a better correlation of simulated with experimental spectra.

Registry No.—**2,** 4054-86-8; **3,** 4118-49-4; **4,** 17290-03-8; **5,** 24694-55-1.

Acknowledgment.—We are indebted to Mr. C. A. Boye of Tennessee Eastman for furnishing us the basic five-spin computer program and to Dr. E. I. Snyder, Visiting Professor of Chemistry, 1969–1970, for rewriting certain segments of this program to fit the (8K) IBM-1130 at East Tennessee State University. We would also like to acknowledge the aid of Mr. Ogawa at JEOLCO for running the 100-MHz spectra. We acknowledge considerable assistance from the East Tennessee State University Research Advisory Council.

Structure of 1,3-Dicyanobicyclo[1.1.0]butane Using X-Ray Analysis

PAUL L. JOHNSON AND JOHN P. SCHAEFER*

Department of Chemistry, University of Arizona, Tucson, Arizona 85721

Received September 28, 1971

Bicyclo[1.1.0]butane and its derivatives are of current interest because of the favorable properties of some of the polymers formed. The structure of bicyclobutane has been assessed using a wide variety of physical methods, including infrared and Raman spectroscopy,[1] microwave spectroscopy,[2,3] electron diffraction,[4] and nuclear magnetic resonance spectroscopy.[5,6] The instability of bicyclobutane makes X-ray diffraction analysis on this compound difficult. However, a substituted bicyclobutane, 1,3-dicyanobicyclobutane (I), is a solid at room temperature and is stable for a sufficient time to collect X-ray data. We wish to report the results of a single-crystal X-ray determination of this substituted bicyclobutane which was kindly supplied to us by Dr. S. C. Cherkofsky of the Du Pont Company.

Experimental Section

Compound I crystallizes as colorless needles elongated about the *b* crystallographic axis. The lattice constants, as determined by a least-squares analysis on the settings for the angles on a four-angle diffractometer for six reflections (Cu K_α, λ = 1.54178 Å) are a = 10.397 (7), b = 5.813 (4), c = 9.358 (8), V = 566 (2) $Å^3$. The systematic absences, $0kl$ when $k = 2n + 1$, $h0l$ when $l = 2n + 1$, $hk0$ when $h + k = 2n + 1$, $h00$ when $h = 2n + 1$, $0k0$ when $k = 2n + 1$, and $00l$ when $l = 2n + 1$, determine the space group to be *Pbcn*. The molecular weight, $C_6N_2H_4$, is 104; $F(000)$ is 216. The observed and calculated densities are 1.20 and 1.22 g cm^{-3}, respectively.

All data in the 2θ range 0–120° were collected with a Picker FACS-I diffractometer. A θ–2θ scan was used; the scan rate was 2 deg/min and 10-sec backgrounds were collected before and after each scan. There were 425 unique reflections of which 321 were considered to be above backround using the criteria $I > 3\sigma(I)$. Lorentz and polarization factors were applied but no absorption corrections were made. The maximum and minimum transmission factors to be applied to the intensities are estimated to be 0.97 and 0.94. A standard reflection was measured every 50th reflection. The intensity of the standard at the end of data collection was 81% of the original. This was corrected for by assuming that the decline in intensity for all reflections followed the decline of the standard. A linear interpolation between each pair of standards was used to arrive at the individual reflections scale factor.

The structure was solved using Long's program for the reiterative application of Sayre's equation.[7] The first E map yielded the positions of all nonhydrogen atoms. After full matrix least-squares refinement, the hydrogen atoms were located from a difference map. Further refinement with carbon and nitrogen vibrating anisotropically while hydrogen vibrated isotropically yielded a final R value of 0.057. The final atomic coordinates are given in Table I and the thermal parameters are in Table II.

TABLE I

FINAL ATOMIC COORDINATES OF DINITRILE BICYCLOBUTANE IN FRACTIONS OF THE UNIT CELL EDGE, WITH STANDARD DEVIATIONS IN PARENTHESES

	x	y	z
N-1	0.3506 (3)	0.5118 (6)	0.0813 (4)
C-2	0.3940 (3)	0.3523 (6)	0.1321 (4)
C-3	0.4492 (3)	0.1507 (5)	0.1929 (3)
C-4	0.4218 (4)	0.0515 (6)	0.3355 (4)
H-5	0.417 (3)	−0.124 (7)	0.340 (4)
H-6	0.367 (3)	0.130 (6)	0.406 (3)

TABLE II

FINAL ANISOTROPIC THERMAL PARAMETERS FOR THE NONHYDROGEN ATOMS EXPRESSED AS $\exp -(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + 2b_{12}hk + 2b_{13}hl + 2b_{23}kl)$. FINAL ISOTROPIC TEMPERATURE FACTORS FOR THE HYDROGEN ATOMS ($B_\theta Å^2$)

	$b_{11}(\times 10^4)$	$b_{22}(\times 10^4)$	$b_{33}(\times 10^4)$	$b_{12}(\times 10^4)$	$b_{13}(\times 10^4)$	$b_{23}(\times 10^4)$
N-1	160 (4)	485 (13)	291 (7)	48 (7)	8 (4)	132 (7)
C-2	121 (4)	396 (13)	171 (5)	−10 (6)	3 (3)	31 (7)
C-3	123 (4)	293 (10)	133 (4)	−6 (5)	−14 (3)	0 (5)
C-4	154 (5)	360 (13)	146 (5)	−47 (6)	5 (4)	18 (7)

	$B\theta$
H-5	7.3 (9)
H-6	5.0 (7)

Results and Discussion

The bond lengths are given in Figure 1 and the bond angles are given in Table III. Most of the parameters found in this study are in agreement with the results of previous structural studies using other methods.[1-6] A notable difference comes in the dihedral angle formed

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