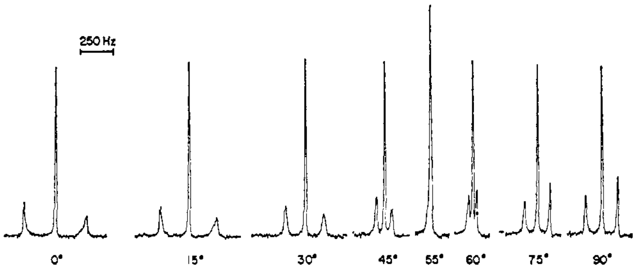

Figure 1. ^{19}F nmr spectrum of 1,1,1-trifluorotrichloroethane oriented in a smectic liquid crystal solvent at 50°. The spectra were measured at several angles with respect to the initial direction (0°) along which the sample was oriented.

ethane (TTE) in *p*-(*p*-2-*n*-propoxyethoxybenzylideneamino)acetophenone[6] was used. Differential scanning calorimetry and microscopic studies show unequivocally that the liquid crystal solvent exhibits only a smectic mesophase.[6] The sample was oriented by cooling from the isotropic melt in the presence of a magnetic field, and ^{19}F magnetic resonance was used to detect and measure the orientation of TTE.

A single sharp resonance is obtained when the sample is in the isotropic state (>63°). Upon cooling into the smectic phase, the intensity of this line decreases, and a diffuse triplet appears. As the temperature is lowered, the outer peaks move away from the center, and the triplet structure becomes more sharply defined. At 50°, the spectrum labeled 0° in Figure 1 is obtained. The triplet is characteristic of the anisotropic dipolar splitting among three equivalent spin $^1/_2$ nuclei located at the vertices of an equilateral triangle, and is observed only when the triangle (in this case, the FFF plane) is oriented.[7]

In the analysis which follows, it is assumed that upon cooling the solvent achieves orientation with its optic axis parallel to the external field, and ordering of the solute follows as a result of solute–solvent interactions. Since the same ordering mechanism is presumed to be operative in nematic solutions, the separation between the outer peaks in the TTE triplet can be written[1a]

$$\Delta\nu = 3\gamma_F{}^2\hbar|S_\alpha|/2\pi r_{FF}{}^3 \text{ Hz} \qquad (1)$$

where γ_F is the fluorine gyromagnetic ratio, and r_{FF} is the interfluorine distance. S_α describes the orientation of the symmetry axis of TTE (along the C–C bond) with respect to the external field, and is given by

$$S_\alpha = (3 \cos^2 \alpha - 1)S_0/2 \qquad (2)$$

where α is the angle between the magnetic field and the smectic optic axis. S_0 is a measure of the ordering of the solute by the oriented solvent.

It is clear from the spectra in Figure 1 that the outer lines are not sharp as in nematic solutions; this is interpreted as a distribution in orientations of the TTE molecules.[8] The validity of eq 1 and 2 can be checked by measuring $\Delta\nu$ as a function of α. This is done by turning the nmr tube, which is equivalent to rotating the sample about an axis perpendicular to the external field direction (for the resulting spectra, see Figure 1). As the sample is turned, the outer lines move in toward the center and, at 55°, coalesce under the center peak. At 90°, the splitting is exactly one-half that measured at 0°, and the intensities confirm that the outer lines have switched position relative to the center. All these observations are consistent with the angular dependence expressed in eq 2, and the splitting between the satellite maxima follows the relation

$$\Delta\nu_{\max} = 230(3 \cos^2 \alpha - 1) \text{ Hz} \qquad (3)$$

From eq 1, an assumed molecular geometry,[9] and the splitting at $\alpha = 0°$, S_0 is found to be 0.0148. This is similar in magnitude to ordering factors for TTE in nematic solutions.[10]

Perhaps the most useful property of smectic solutions is that the external field is no longer necessary to maintain the orientation, once the sample has been prepared. As an illustration, the sample was taken out of the gap, and kept at 50° for 96 hr without any observable change in the orientation. In conclusion, it is felt that smectic solvents may prove to be the most versatile liquid crystal matrix for orienting molecules, and that the advantage of field-independent orientation in the bulk may be realized in a wide variety of experiments designed to measure phenomena in which molecular ordering plays a role.

Acknowledgments. The author acknowledges the able assistance of Mr. John V. Powers, who prepared the sample and obtained some of the nmr spectra.

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[6] The author thanks Mr. R. J. Cox, of the IBM San Jose Laboratory, for making some of this material available, and Dr. I. Haller of this laboratory for the results of his phase-transition studies.

[7] A. Saupe and J. Nehring, *J. Chem. Phys.*, 47, 5459 (1967).

[8] Studies of possible orientation distributions consistent with the observed spectra are currently being made.

[9] L. E. Sutton, "Tables of Interatomic Distances and Configurations in Molecules and Ions," Burlington House, London, 1958, p M128.

[10] C. S. Yannoni, to be submitted for publication.

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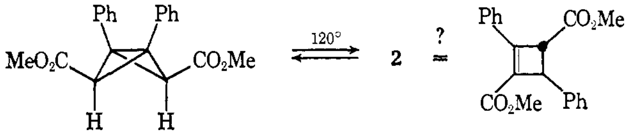
Received June 9, 1969

Dimethyl 1,3-Diphenylbicyclobutane-2,4-dicarboxylates

Sir:

In 1966 the thermal equilibration of dimethyl 1,3-diphenylbicyclobutane-2,4-dicarboxylate (**1**) and dimethyl 2,4-diphenylcyclobutene-1,3-dicarboxylate (**2a**) was reported.[1] Several facts led us to question the structure (**2a**) assigned to the isolated compound (**2**),



1

2a

mp 118–119°. Among these were the observations that the equilibrium only slightly favored the presumably much more stable isomer (**2a**),[1a,2] and that the two unique protons in **2** have identical chemical shifts (δ 4.26, $CHCl_3$, TMS).[1b] A third objection to structure **2a** is mechanistic, considering the contortions that **1** must undergo during the isomerization. It has been suggested[3] that structure **2b** better accounts for the experimental data; however, it is difficult to see why **2b**

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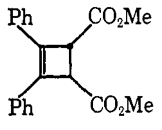
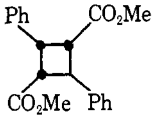
[1] (a) I. A. D'yakonov, V. V. Razin, and M. I. Komendantov, *Tetrahedron Letters*, 1135 (1966); (b) *ibid.*, 1127 (1966).

[2] $\Delta H_f°$ (bicyclobutane–cyclobutene) = 14.4 kcal/mole: K. B. Wiberg and R. A. Fenoglio, *J. Am. Chem. Soc.*, 90, 3395 (1968).

[3] K. B. Wiberg, *Tetrahedron*, 24, 1083 (1968).



2b



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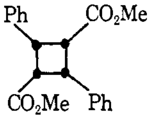

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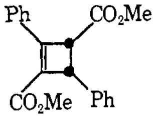


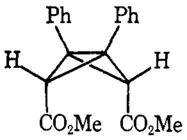
2c

should not also be of much lower energy than **1**. Structure **2b** also fails to explain the reported formation of dimethyl γ-truxillate (**3**) by catalytic hydrogenation of **2**.[1b] This fact was seemingly incontrovertible evidence for structure **2a**. The ultraviolet spectrum of **2** (λ_{max} 270 mμ)[1b] was also not typical of 1,2-diphenylcyclobutenes (λ_{max} 297–305 mμ).[4] With this background of facts and speculation a study was begun of this novel isomerization of **1**.

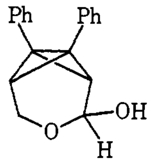
Compounds **1** and **2** were prepared and isolated by the procedure of D'yakonov and coworkers, and their physical and spectral properties were in close agreement with the data reported.[1b] To determine whether the nmr spectrum of **2** (in $CHCl_3$) was the result of coincidental chemical shifts of nonidentical protons (as in **2a**), the spectrum was recorded in several other solvents (C_6H_6, CCl_4, C_2Cl_4, C_5H_5N). Although the methoxyl proton signal varied from δ 3.50 to 3.74 and the two-proton signal from δ 4.06 to 4.79, in each of the solvents both signals appeared as sharp, ringing singlets, suggesting some structure with more symmetry than **2a**.

The first hint of a solution to the dilemma came following catalytic hydrogenation of **2**. Using 10% Pd–$CaCO_3$ (ethyl acetate, room temperature, 1 atm of H_2), **2** was reduced cleanly to dimethyl η-truxillate (**4**), *not* the γ isomer (**3**).[5] Both the γ and η isomers were synthesized by literature procedures[6] and were identified by melting point and nmr spectra: γ isomer (**3**), mp 127–128° (lit.[6] 127°); nmr ($CDCl_3$, TMS internal) δ 7.33 (5 H, s), 7.28 (5 H, s), 4.81 (1 H), 4.20 (1 H), 3.70 (2 H), 3.37 (6 H, s); the ring protons appeared in an ABC_2 pattern, $J_{AB} = 0$ Hz, $J_{AC} = 10.8$ Hz, $J_{BC} = 10.3$ Hz; η isomer (**4**), mp 102.5–103.5° (lit.[6] 104.5°); nmr ($CDCl_3$, TMS) δ 7.24 (10 H, s), 4.33 (2 H), 4.10 (2 H), 3.49 (6 H, s); the ring protons appeared in an A_2B_2 pattern, $J_{AB} = J_{AB'} = 9.5$ Hz. The hydrogenation product was definitely dimethyl η-truxillate as judged by comparisons of melting point and nmr, ir, and mass spectra.

While **4** could certainly result from the hydrogenation of the *cis*-substituted cyclobutene **2c**, most of the objections to structure **2a** apply equally to **2c**. The *only* structure for compound **2** which can account for *all* of the above observations is the *endo,endo* isomer of **1**, *i.e.*, **2d**. The reduction to dimethyl η-truxillate is by hydrogenolysis of the 1,3 bond in **2d**; **1** and **2d** may be of comparable stability (*vide infra*); the two ring protons are identical; and thermal interconversion of **1** and **2d** is easily accomplished by breaking the 1,3 bond as in the well-studied isomerizations of bicyclo[2.1.0]pentanes.[7,8] Proof that **4** was formed by hydrogenolysis of **2d**, rather than hydrogenation of **2c**, was provided by nmr and mass spectral analyses of the product of the reduction of **2** with D_2. The nmr spectrum showed only one type of ring proton in **4** (δ 4.10, s), and the mass spectral fragmentation indicated that the two deuterium atoms in **4**-d_2 were on opposite rather than adjacent carbon atoms in the cyclobutane.[9]



2d



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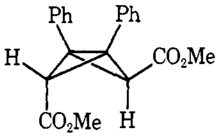

6

D'yakonov and coworkers[1b] assigned the *exo,exo* stereochemistry to **1** assuming that only one symmetrical isomer was formed and that the *endo,endo* isomer would be less stable due to crowding of the *endo* ester groups. Since compound **2** is slightly more stable than **1** (K_{eq} = 1.40 ± 0.07),[10] the question arises whether the assignments given above ought to be reversed. That those assigned are in fact correct was shown by the controlled reduction of **2** with $LiAlH_4$ (0°, Et_2O) to the hemiacetal (**5**) in 80% yield; mp 148–52°; mass spectrum, *m/e* 264 (m^+, $C_{18}H_{16}O_2$, 15%), 218 (m^+ − HCOOH, 100%, m^* 180); ir 3630, 1018 (R_2CHOH), 1108 cm^{-1} (C–O–C); uv λ_{max}^{MeOH} 218 mμ (log ϵ 4.09), 274 mμ (log ϵ 4.09); the nmr spectrum of **5** was complex, but consistent with the assigned structure.

The only remaining question concerns the uv spectrum of **2** [λ_{max}^{MeOH} 219 mμ (log ϵ 4.22), 269 mμ (log ϵ 4.13)]. Neither **1** [λ_{max}^{MeOH} 221 mμ (log ϵ 4.12)] nor the *exo,endo* isomer **6**[1] [λ_{max}^{MeOH} 220 mμ (log ϵ 4.10)] shows an absorption maximum comparable to the 269-mμ band of **2**. Indeed the lack of such absorption was used by D'yakonov and coworkers as evidence for the bicyclobutane structures.[1b] On surveying the literature of 1,3-diphenylbicyclobutane derivatives,[11] it appears rather that **1** and **6** are exceptional in lacking a long wavelength maximum, and that **2** is quite normal; *e.g.*, methyl 1,3-diphenylbicyclobutane-*endo*-2-carboxylate has λ_{max} 270 mμ.[11a] An explanation of this anomaly and a more detailed description of the isomerizations of **1**, **2**, and **6** will be reported in full on completion of work in progress.

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[4] H. H. Freedman and A. M. Frantz, Jr., *J. Am. Chem. Soc.*, **84**, 4165 (1962); R. M. Dodson and A. G. Zielske, *J. Org. Chem.*, **32**, 28 (1967).

[5] Reduction over Pt, as described by D'yakonov, *et al.*,[1b] in our laboratory failed to stop after uptake of 1 equiv of H_2, and no truxillic esters could be found in the product mixture.

[6] R. Stoermer and F. Bacher, *Ber.*, **57**, 15 (1924).

[7] J. P. Chesick, *J. Am. Chem. Soc.*, **84**, 3250 (1962).

[8] Preliminary kinetic investigations of the $1 \rightleftharpoons 2$ isomerization indicate that $\Delta H^{\ddagger} = 26 \pm 2$ kcal/mole and $\Delta S^{\ddagger} = 9 \pm 4$ eu.

[9] This determination was possible since the major fragmentation pathway of the truxillic esters is *via* cleavage to a methyl cinnamate ion.

[10] As measured by nmr in C_2Cl_4 at 90–130°. The derived thermodynamic constants are $\Delta H = 0 \pm 1$ kcal/mole and $\Delta S = 1 \pm 2$ eu.

[11] (a) S. Masamune, *Tetrahedron Letters*, 945 (1965); (b) S. Masamune, *J. Am. Chem. Soc.*, **86**, 735 (1964); *cf.* W. von E. Doering and M. Pomerantz, *Tetrahedron Letters*, 961 (1964); (c) A. S. Monahan, *J. Org. Chem.*, **33**, 1441 (1968).

[12] A portion of this work was carried out during the tenure of a postdoctoral fellowship from the National Science Foundation. This investigation was also supported in part by a grant from the National Institutes of Health.

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Received May 16, 1969