Communications to the Editor

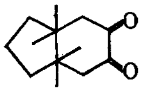
A Rigid, Internally Saturated Derivative of Cyclononane

Sir:

Although conformational molecular dissymmetry in saturated nine-membered carbocycles was postulated about 30 years ago,[1] efforts to demonstrate the phenomenon *via* classical procedures of resolution and isolation of stable, optically active enantiomorphs have been unsuccessful.[2] Even in the highly substituted systems examined, ring inversion with concomitant racemization was apparently very rapid. In contrast to the foregoing, Cope and his associates have shown molecular dissymmetry in several medium-sized *trans*-cycloalkenes.[3]

With the diketone 4,4,8,8-tetramethyl-1,2-cyclononanedione (**1**) available as a precursor for a number of derivatives, continuation of studies directed toward a realization of stable dissymmetric cyclononanes was encouraged. Acyloin cyclization of dimethyl $\beta,\beta,\beta',\beta'$-tetramethylazelate followed by cupric acetate oxidation[2c] affords the α-diketone **1** (83% yield): mp 60–61°; ir (CCl_4) 3.38, 5.90, 6.82, and 10.08 μ; nmr (CCl_4, 25°) τ 7.51 (s, 4 H), 8.65–8.78 (m, 6 H), and 8.98 (s, 12 H). Low-temperature nmr studies of **1** in methylene chloride down to −80° showed no significant change in the spectrum other than a general broadening due to increased viscosity of the solution. The simplicity of the spectrum of this relatively complex molecule indicates that ring inversion, accompanied by time averaging, is rapid even at low temperatures.

Upon heating the diketone **1** with 85% hydrazine hydrate in absolute ethanol for 5.5 hr, removing of solvent, and recrystallizing from hexane, the pure dihydrazone (tlc analysis), 4,4,8,8-tetramethyl-1,2-cyclononanedione dihydrazone (**2**), was obtained in 64.3% yield: mp 130–133° dec; ir (KBr) 2.94, 3.09, 3.39, 6.12, 6.31, and 6.80 μ. *Anal.* Found: C, 65.38, 65.47; H, 10.98, 10.89; N, 23.65, 23.51; mol wt, 234, 240. In contrast to the relatively simple and temperature-independent nmr spectrum of the α-diketone **1**, that of the dihydrazone **2** was totally unexpected: nmr ($CHCl_3$) τ 4.64 (s, 4 H), 7.76 (AB q, 4 H, $J = 14.5$ Hz), 8.49–8.78 (m, 6 H), 8.98 (s, 6 H), and 9.09 (s, 6 H). The nmr spectrum supports two important conclusions: (1) ring inversion at room temperature must be slow to give rise to two magnetically nonequivalent methyl signals of equal area together with a four-proton AB quartet (methylene protons α to the hydrazone functions), and (2) the α-dihydrazone functions must possess the *syn,syn* or *anti,anti* configuration but not the *syn,anti* arrangement.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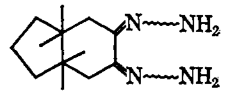

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For purposes of analysis the skeletal arrangement of cyclononylamine hydrobromide, as determined by X-ray analysis,[4] was selected as the most suitable model for nine-membered carbon rings.[5] Accordingly, when the dihydrazone **2** is constructed to correspond as closely as possible to the X-ray model (*supra vide*) and with the geminal methyl groups restricted to positions that contain no intraannular hydrogen atoms, the two adjacent trigonal carbon atoms effect destruction of the basic skeletal asymmetry and create a C_2 axis running through C-6 and bisecting the 1,2 bond.[7] The model predicts correctly the observed nmr spectrum provided ring inversion is slow. Since it is unlikely that the basic ring conformation is changed in the conversion of the α-diketone **1** to the dihydrazone **2**, the uv spectrum of **1** affords a qualitative check on the applicability of the model.

The uv spectrum of the α-diketone **1** shows a long-wavelength absorption ("A band") at 375 mμ in ethanol. On the basis of the data reported by Leonard,[9] this places the dihedral angle between the carbonyl groups in the diketone **1** roughly in the range 95–180°.[10] Examination of the model based on the X-ray analysis gives a similarly large value for the dihedral angle.[12]

Although the nmr spectrum of the dihydrazone **2** at room temperature certainly implies that the ring inversion is slow, ultimate verification must be provided by temperature variance of the spectrum; rapid ring inversion at higher temperatures should collapse the AB quartet and lead to the appearance of a single methyl signal. Examination of the nmr spectrum of the dihydrazone **2** in diglyme at higher temperatures showed that (a) at 73° there was no change, (b) at 104° the methyl peaks began to broaden and the relative height of the peak due to the ring methylenes became greater than either of the methyl signals, and (c) at 130° the

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(1) C. S. Marvel and D. B. Glass, *J. Am. Chem. Soc.*, **60,** 1051 (1938).

(2) (a) A. T. Blomquist, E. S. Wheeler, and Y. Chu, *ibid.*, 77, 6307 (1955); (b) A. T. Blomquist and Y. C. Meinwald, *J. Org. Chem.*, **23,** 6 (1958); (c) A. T. Blomquist and G. A. Miller, *J. Am. Chem. Soc.*, **83,** 243 (1961).

(3) (a) A. C. Cope, C. R. Ganellin, H. W. Johnson, Jr., T. V. van Auken, and H. J. S. Winkler, *ibid.*, **85,** 3276 (1963); (b) A. C. Cope, K. Bankolzer, H. Keller, B. A. Pawson, J. J. Whang, and H. J. S. Winkler, *ibid.*, **87,** 3644 (1965); (c) A. C. Cope, J. K. Hecht, H. W. Johnson, Jr., H. Keller, and H. J. S. Winkler, *ibid.*, **88,** 761 (1966).

(4) R. F. Bryon and J. D. Dunitz, *Helv. Chim. Acta*, 43, 3 (1960).

(5) The evidence in support of the applicability of conformational preferences of medium-sized rings as determined by the X-ray analysis of solid derivatives to similar molecules in the liquid state or in solution has been summarized by Prelog.[6]

(6) V. Prelog, Proceedings of the Robert A. Welch Foundation, Vol. IV, Houston, Texas, 1961, p 43.

(7) This is based on the premise that the introduction of *exocyclic* double bonds should not change the basic conformational skeleton as suggested by Pitzer.[8]

(8) K. S. Pitzer and W. E. Donath, *J. Am. Chem. Soc.*, **81,** 3213 (1959).

(9) N. T. Leonard and P. M. Mader, *ibid.*, 72, 5388 (1950).

(10) The enol content of **1**, although not detectable by ir or nmr spectroscopy, probably contributes to the ultraviolet spectrum due to the increased sensitivity of the instrument. This, however, should not interfere with the observation of the long-wavelength band since the uv spectra of enolic α-diketones is essentially that of an α,β-unsaturated carbonyl compound with strong absorption occurring at much shorter wavelengths.[11]

(11) (a) H. S. French and M. E. T. Holden, *J. Am. Chem. Soc.*, **67,** 1239 (1945); (b) E. T. Stiller and O. Rosenheim, *J. Chem. Soc.*, 353 (1938).

(12) Although this model is both convenient and nicely rationalizes the experimental data, its adoption is not essential to demonstrate ring rigidity.

methyl peaks collapsed into a broad singlet and the AB quartet was no longer recognizable as such. (Unfortunately, at ~130° slight decomposition began to occur and a second peak appeared on the side of the broad methyl signal.) By 142° the AB quartet had collapsed to a singlet and the methyl groups appeared as a relatively sharp single peak with the signal from the impurity still clearly visible on the side of the methyl signal. Finally, return to room temperature effected a regeneration of the AB quartet and the two methyl signals at τ 8.98 and 9.09; the presence of the impurity from the thermal decomposition was indicated by a peak between the two sharp methyl singlets.[13] These nmr studies at various temperatures indicate that there is some process operative at high temperatures that causes the equivalence of two otherwise magnetically nonequivalent methyl groups. This process is considered to be rapid ring inversion with its resultant time-averaging effect.[14]

In view of the interesting result reported, other derivatives of the α-diketone **1**, which should be less thermally labile than the dihydrazone **2**, are being prepared for purposes of kinetic measurements and possible resolution into optical isomers.

[13] An analogous situation has been observed by Prelog and coworkers in a number of similarly substituted cyclodecane derivatives, but in each case the coalescence temperature was much lower, reflecting the lower barrier to inversion in the ten-membered ring. We are indebted to Professor Prelog for this private communication.

[14] This is not to imply that the stereochemical integrity of the hydrazone functions in the starting material is maintained at high temperatures for there may well be rapid interconversion between stereoisomers, but this phenomenon, however rapid, cannot alone cause the observed collapse of the spectrum without concurrent ring inversion.

[15] Sage Teeple Fellow, 1965–1966, and National Institutes of Health Predoctoral Fellow, 1966–1967.

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Tin-119m Mössbauer Study of Five- and Six-Coordinated Organotin(IV) Ions

Sir:

The addition of 2,2′,2′′-terpyridyl to dimethyltin dichloride in hexane precipitates an adduct which behaves as a 1:1 electrolyte in nitrobenzene.[1] The formulation of the product as $[Me_2SnCl\cdot terpy]^+[Me_2SnCl_3]^-$ (I) has been confirmed by an X-ray study.[2] The coordination about the tin in the anion is trigonal bipyramidal with the methyl groups in equatorial positions. The cation is a highly distorted octahedron with bent *trans*-methyl groups. The Sn^{119m} Mössbauer spectrum is shown in Figure 1.

A doublet spectrum is consistent with the proposals of Greenwood, *et al.*, that organotin(IV) compounds will exhibit resolvable quadrupole splittings (QS) when the symmetry about the tin atom is lower than cubic so long as at least one bond to tin is from an element possessing a lone pair of electrons.[3,4] Thus both types of tin atoms in the adduct (the five-coordinated anion and the six-coordinated cation) must be giving rise to isomer shift (IS) and QS values sufficiently similar to allow their respective resonances to fall within the envelope of the doublet produced with the narrow-line $BaSn^{119m}O_3$ source.[5]

The IS value is smaller than that for the neutral Me_2SnCl_2 precursor. We find this observation to be general in going to five- and six-coordinated species whether charged or not. The IS for tin can be expressed as

$$\mathrm{IS} = \mathrm{constant}\,[\rho_a - \rho_s]$$

where ρ, the total electric field at the nucleus for source and absorber, is usually replaced by $|\Psi(0)|^2$, the total electron density at the nucleus, and then by $|\psi_{ns}(0)|^2$, the total s-electron density at the tin nucleus. Populating empty tin 5d orbitals on coordination will affect the s-electron distribution by shielding so as to lower $|\psi_{ns}(0)|^2$.

Table I lists IS and QS data for various five- and six-coordinated organotin(IV) anions and cations.[6] Half-height widths are listed for each resonance line. The results for the separated ions of $[Me_2SnCl\cdot terpy]^+$-$[Me_2SnCl_3]^-$ with various gegenions confirm that Figure 1 represents the superimposition of the doublet spectrum arising from each tin atom and rule out the possibility that interionic interaction (for example, the presence of a bridging chlorine atom not specifically excluded in ref 2) might be operating to bring the two tin atoms into electrical and stereochemical equivalence in the mixed salt. The intensities of the resonances produced by the tin anion and cation, although in general not equal, are of the same order of magnitude. Thus the effective Debye temperatures and binding force constants of the two types of tin atoms are, therefore, comparable and both tin atoms must be represented in Figure 1. This pattern of results is repeated for the complex ions formed from diphenyltin dichloride, methyl- and butyltin trichlorides, as well as from tin tetrachloride itself. In each case formation of the complex moves the IS to lower values, but both types of tin atoms give rise to IS and QS values which allow their resonances to fall within a single envelope. It should be noted that methyl- and butyltin trichlorides precipitate 2:1 electrolytes with a six-coordinated $[RSnCl_5]^{2-}$ dianion. Tin tetrachloride likewise precipitates a 2:1 electrolyte,[7] but in this case the dianion possesses cubic symmetry and for the cation the Greenwood proposals predict a singlet spectrum.[3,4] We observe the apparent superimposition of the two singlet resonances.

We expected little or no decrease in IS in the formation of $[Me_3SnCl_2]^-$ from Me_3SnCl because of the likelihood that Me_3SnCl itself exists in the solid as a pentacoordinated chain polymer.[8] This is suggested by far-infrared and Raman studies which give ν(Sn–Cl) at different frequencies in the solid, melt, and solution,

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[1] J. E. Fergusson, W. R. Roper, and C. J. Wilkins, *J. Chem. Soc.*, 3716 (1965).

[2] F. W. B. Einstein and B. R. Penfold, *Chem. Commun.*, 780 (1966).

[3] T. C. Gibb and N. N. Greenwood, *J. Chem. Soc.*, *A*, 43 (1966).

[4] N. N. Greenwood and J. N. R. Ruddick, *ibid.*, 1679 (1967).

[5] M. V. Plotnikova, K. P. Mitrofanov, and V. S. Shpinel, *Soviet Phys. JETP Letters*, **3**, 209 (1966); H. Sano and R. H. Herber, *J. Inorg. Nucl. Chem.*, 30, 409 (1968).

[6] Various forms of evidence have been put forward recently to support the ionic nature of these species: (a) G. Tagliani, P. Zanella, and M. Fiorani, *Coord. Chem. Rev.*, **1**, 249 (1966); (b) G. Tagliani and P. Zanella, *Anal. Chem. Acta*, 40, 33 (1967); (c) *J. Organometal. Chem.* (Amsterdam), **5**, 299 (1966); (d) M. Wada and R. Okawara, *ibid.*, 4, 487 (1965); (e) V. G. K. Das and W. Kitching, *ibid.*, **10**, 59 (1967).

[7] This species is too insoluble to allow conductivity measurements or the separation of the ions (see ref 1).

[8] H. A. Stöckler, private communication, 1968.