mations corroborated the structure of **3**. Haller–Bauer cleavage with sodium amide led to an amide whose melting point (136.5–138.5°) corresponded to that reported (m.p. 135–136°) for **10**.[16] Conversion of **3** to its *p*-toluenesulfonylhydrazone ($C_{16}H_{20}N_2O_2S$, m.p. 146.5–147.5°) and treatment with sodium methoxide in bis(2-ethoxyethyl) ether[17] gave the tetracyclic hydrocarbon **11**, prepared earlier.[5]

The rearrangement of **1** → **3** under alkaline conditions most reasonably proceeds through the homoenolate ion **2**, formed by abstraction of a hydrogen from C-4 (or from its equivalent position C-9). The driving force in the isomerization may lie in a greater thermodynamic stability of **3**, a factor that could also be of relevance in the solvolysis behavior of compounds with these skeletons.[18]

(16) R. Granger, P. F. G. Nau, and J. Nau, *Bull. soc. chim. France*, 1807 (1959); R. Granger, *et al.*, *ibid.*, 1350 (1960).

(17) L. Friedman and H. Schechter, *J. Am. Chem. Soc.*, **81**, 5512 (1959).

(18) We have also developed routes to the brendane skeleton variously functionalized at C-2 and to the brexane skeleton functionalized at C-4 (i) by homoconjugative Diels–Alder addition of norbornadiene and

R
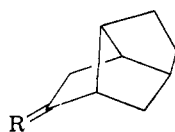
i, R = O
ii, R = H₂

dienophiles such as α-acetoxyacrylonitrile or methyl vinyl ketone followed by conventional transformations to give the tetracyclic hydrocarbon **11**.[5,19] Cleavage of **11** with sulfuric acid in acetic or formic acid followed by saponification of the esters and oxidation of the alcohols led to brendan-2-one (**3**) and brexan-4-one (i; $C_9H_{12}O$, $n^{25}D$ 1.4968, ν 1744 and 1407 cm.⁻¹; semicarbazone $C_{10}H_{15}N_3O$, m.p. 202–204°). Wolff–Kishner reduction of i gave brexane (ii),[5] and Bamford–Stevens reaction[17] on the *p*-toluenesulfonylhydrazone of i ($C_{16}H_{20}N_2O_2S$, m.p. 192–192.5° dec.) regenerated hydrocarbon **11**. Solvolytic and other mechanistic studies with appropriate derivatives of brexane, brendane, and the other ring systems shown are in progress.

(19) H. K. Hall, Jr., *J. Org. Chem.*, **25**, 42 (1960).

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The Conformational Free Energy (ΔG) of the Nitro Group[1]

Sir:

In a recent paper on the proton magnetic resonance spectra of nitroalkanes[2] it was suggested that, under the experimental conditions used, nitrocyclohexane exists solely in the chair conformation with the nitro group equatorial (I, Figure 1). We wish to report that on
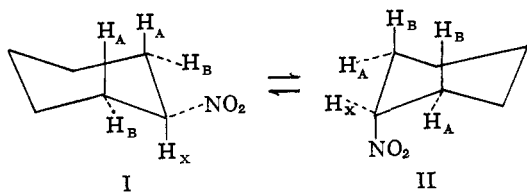
I   II

Figure 1. I. mole fraction = m; II, mole fraction = $(1 - m)$.

(1) Conformational Analysis by Nuclear Magnetic Resonance, Part V. For Part IV, see H. Feltkamp, N. C. Franklin, M. Hanack, and K.-W. Heinz, *Tetrahedron Letters*, 3535 (1964).

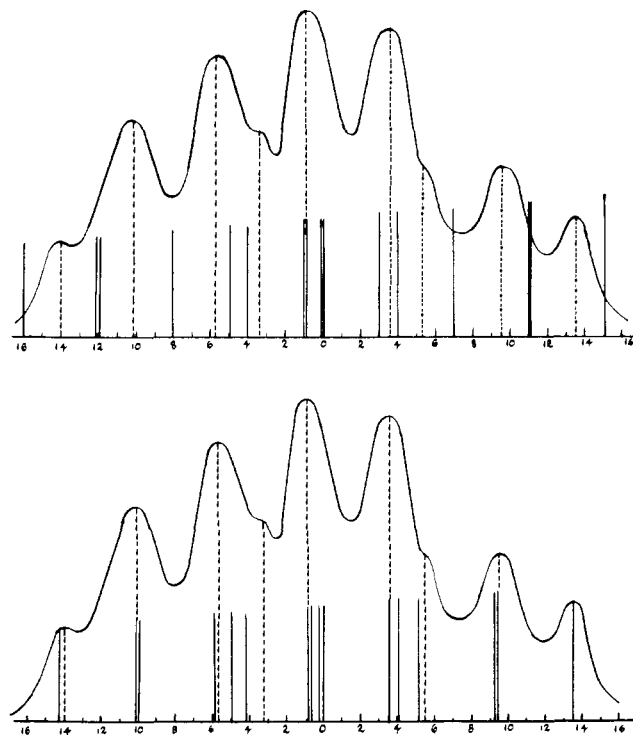(2) W. Hofman, L. Stefaniak, T. Urbanski, and M. Witanowski, *J. Am. Chem. Soc.*, **86**, 554 (1964).

Figure 2. Spectrum 1 (upper) of Urbranski, *et al.*; spectrum 2 (lower) by Feltkamp and Franklin, -------- experimental; ———— theoretical.

further calculation we have found that the nitro group has a conformational free energy (ΔG) of approximately 1 kcal./mole and at room temperature exists as only 85 % in conformer I. Using a method recently developed[3] for measuring the equilibrium constant *K* from the band width of the methine multiplet of the tertiary (X) proton, it has been found that the equilibrium constant may be expressed as

$$K = \frac{w_a - w}{w - w_e} \tag{1}$$

The values of w_e (the band width of the X proton in conformer I) and w_a (the band width of the X proton in conformer II) were obtained from the n.m.r. spectra of *trans*- and *cis*-4-*t*-butyl-1-nitrocyclohexane,[4] respectively. It was found that w_a was 14 ± 0.5 c.p.s.[5] and w_e was 30 ± 0.5 c.p.s., while w (the band width of the X proton of nitrocyclohexane at 26°) was reported as 27.5 ± 0.5 c.p.s.[2] Hence *K* was calculated to be 5.7 ± 1.5, which indicated a mole fraction of 84.5 ± 3 % of conformer I present at 26°. This value of *K* was used to calculate a ΔG value of the nitro group of 1.02 ± 0.15 kcal./mole. As a check of the above results, the method developed by Eliel[6] to calculate the equilibrium constant from the chemical shift of the X proton was used. From eq. 2 and the published

$$K = \frac{\tau_a - \tau}{\tau - \tau_e} \tag{2}$$

(3) H. Feltkamp and N. C. Franklin, *Ann. Chem.*, **683**, 55 (1965).

(4) A. C. Huitric and W. F. Trager, *J. Org. Chem.*, **27**, 1926 (1962).

(5) This value has been calculated from available data on the values of J_{ae} (4.2 c.p.s.) and J_{ee} (2.7 c.p.s.).

(6) E. L. Eliel, E. W. Della, and T. H. Williams, *Tetrahedron Letters*, 831 (1963).

values of τ_a and τ_e (5.57 and 5.77),[4] together with the reported value of τ (5.72 for nitrocyclohexane),[2] an equilibrium constant of 3 was calculated. This latter method is likely to be less accurate in this case, compared to the band-width method, due to the small difference in chemical shift between the equatorial and axial X protons in conformers I and II. However, both methods indicate that approximately 13–25% of conformer II is present in nitrocyclohexane at room temperature.

It now remains to explain why a septet was observed for the X proton in nitrocyclohexane. Recent work[3,7] has shown that interchanging conformations do not show a quintet with coupling constant $J_{av} \approx 7$ c.p.s. (i.e., $J_{av} \neq (J_{aa} + J_{ea})/2$), and in order to calculate the time-averaged coupling constants the method as applied by Booth[7] to mobile cyclohexane systems must be used. Thus the averaged coupling constants are $J_{AX} = mJ_{aa} + (1 - m)J_{ee}$, and $J_{BX} = mJ_{ea} + (1 - m)J_{ae}$.

It has recently been shown that in a *fixed* cyclohexyl system containing a nitro group the coupling constants are $J_{aa} = 11.0–11.5$ and $J_{ea} = 4.0–4.2$[8] c.p.s. Unfortunately, as yet no value of J_{ee} for nitro systems has been measured; however, it was reasonable to assume that $J_{ee} = 2.7$ c.p.s.[9] as used in calculating w_a. It was also assumed for the present that $J_{ea} = J_{ae}$, although it has been pointed out that this need not necessarily be so.[10] With these assumptions it was calculated that $J_{AX} = 9.95 \pm 0.45$ c.p.s. while $J_{BX} = 4.1 \pm 0.1$ c.p.s. It was then observed that these *average* coupling constants were very close to the coupling constants used by Urbanski[2] to calculate the theoretical spectrum. For this reason, among others, a very good agreement was found between the experimental and theoretical spectra. However, if the theoretical spectrum for a fixed system was recalculated using the *fixed* coupling constants (and correcting the mathematical mistakes in Table 1 of Urbanski's paper[2]), it was seen that there was very poor agreement with the experimental curve (spectrum 1 of Figure 2). However, using the average coupling constants[11,12] it was observed from spectrum 2 (Figure 2) that these fit the experimental curve more accurately.[13]

It is of interest at this point to comment on the results of Neikam and Dailey[14] for nitrocyclohexane. On cooling, no separation of the methine (X) proton into its axial and equatorial components was observed. This is most likely due to the very small chemical shift (τ 0.2) between the two components; however, it is possible, if extremely low temperatures are used, that such a splitting may be observed. Against this though is the fact that assuming the ΔG value of the

(7) H. Booth, *Tetrahedron*, 20, 2211 (1964).
(8) A. C. Huitric, J. B. Carr, W. F. Trager, and B. J. Nist, *ibid.*, 19, 2145 (1963).
(9) F. A. L. Anet, *J. Am. Chem. Soc.*, 84, 1053 (1962).
(10) D. H. Williams and N. S. Bhacca, *ibid.*, 86, 2742 (1964).
(11) The second-order perturbation method[12] was used with the constants $\gamma_A = \tau$ 5.72, $\gamma_B = \tau$ 8.00, $\gamma_C = \tau$ 8.20,[13] $J_{AC} = 9.7$ c.p.s., $J_{AB} = 4.2$ c.p.s.
(12) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, pp. 151–156.
(13) Values of γ_B and γ_C were taken from 3-nitropentane, as it was believed that a straight chain nitroalkane does not provide the best model for nitrocyclohexane. The differences, however, lie within the limits of experimental accuracy.
(14) W. C. Neikam and B. P. Dailey, *J. Chem. Phys.*, 38, 445 (1963).

nitro group as approximately 1 kcal./mole, then at $-75°$ only 8.5% of nitrocyclohexane would exist with the nitro group axial, and thus the equatorial hydrogen signal is liable to be very small and perhaps not observed. As proof of this suggestion it may be mentioned that no splitting was observed on cooling cyclohexylamine,[14] although it is known that the ΔG value of the amino group is 1.2 kcal./mole.[15] This would, however, give only 7% of axial amine at $-75°$.

Further studies are in progress on the synthesis of a number of nitro compounds with a view to determining more accurately the conformational free energy of this group, and the results will be published in due course.

(15) H. Feltkamp, N. C. Franklin, and K. D. Thomas, *Ann. Chem.*, 683, 64 (1965).
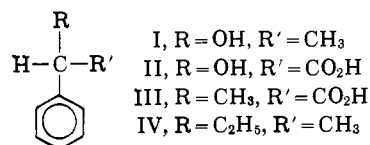(16) NATO Postdoctoral Research Fellow, 1963–1965.

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The Benzene Ring as an Optically Active Chromophore

Sir:

Although the carbonyl group has proved to be extremely useful as an optically active chromophore in optical rotatory dispersion (o.r.d.) studies,[1] increasing attention is being given to compounds possessing other chromophoric groups. Because of conflicting reports in the literature concerning the behavior of a benzene ring attached to an asymmetric carbon center we have undertaken a study of this chromophore.

An o.r.d. investigation of methylphenylcarbinol (I) and its derivatives led Kuhn and Biller[2] to the conclu-

sion that the benzene absorption band in the 260 mμ region of this compound is not optically active. On the other hand, several derivatives of mandelic acid (II) showed anomalous rotatory dispersion in the benzene absorption region.[2] Sjöberg[3] was able to observe the peak of a Cotton effect at 270 mμ for atrolactic acid (III) although this wave length was close to the limit of his instrument. Lyle[4] has shown that in certain amines and alcohols having a benzene ring attached to the asymmetric center, the aromatic group exhibits a Cotton effect. The results of calculations utilizing the Drude equation led to the conclusion that the aromatic ring of steroids such as estradiol is optically active.[5] L-Tyrosine, in which the phenolic ring is one carbon removed from the asymmetric center, displays a Cotton effect associated with the aromatic absorption band near 280 mμ.[6] In contrast, the aromatic absorp-

(1) C. Djerassi, *Proc. Chem. Soc.*, 314 (1964).
(2) W. Kuhn and H. Biller, *Z. physik. Chem.*, B29, 1 (1935).
(3) B. Sjöberg, *Acta Chem. Scand.*, 14, 273 (1960).
(4) G. G. Lyle, *J. Org. Chem.*, 25, 1779 (1960).
(5) E. W. Foltz, A. E. Lippmann, and C. Djerassi, *J. Am. Chem. Soc.*, 77, 4359 (1955).
(6) T. M. Hooker and C. Tanford, *ibid.*, 86, 4989 (1964).