

II is $1.0 \times 10^{-9} \text{ sec}^{-1}$ at 25° . This leads to a ratio of rates of reaction of $10^7:1$ for I and II. Since the same product is formed from each compound, it is clear that thermodynamic factors are not involved in the difference in reactivity.

The rate of reaction of II is similar to that of *t*-butyl 3,5-dinitrobenzoate ($k_{110} = 4.31 \times 10^{-5} \text{ sec}^{-1}$) and spiro[4.2]-2-heptyl dinitrobenzoate ($k_{110} = 2.70 \times 10^{-4} \text{ sec}^{-1}$).⁶ It also appears to be essentially the same as that for northujyl *p*-nitrobenzoate.⁷ The reactivity of II is then normal for a secondary cyclopropylcarbonyl derivative.

The marked acceleration found with I must be due to strain relief in the activated complex. The difference in activation enthalpy between I and II (12 kcal/mol) is nearly half the strain relief on going from bicyclo[2.1.0]pentane to cyclopentene.⁸ Thus, the process depicted above must have occurred to a large extent in the formation of the activated complex for I. The experimental results are then in excellent agreement with the expectations based on the orbital participation scheme.

(6) K. B. Wiberg and J. E. Hiatt, *Tetrahedron Letters*, 3009 (1968).

(7) From the data given by L. Birlindeanu, T. Hanafusa, B. Johnson, and S. Winstein, *J. Am. Chem. Soc.*, **88**, 2316 (1966); we estimate a rate constant of $1 \times 10^{-9} \text{ sec}^{-1}$ at 25° .

(8) From the heat of hydrogenation of bicyclopentane (R. B. Turner, "Kekule Symposium," Butterworth & Co. (Publishers) Ltd., London, in press, p 67) one obtains $\Delta H_f^\circ = 36.6 \text{ kcal}$ whereas $\Delta H_f^\circ = 7.9 \text{ kcal}$ for cyclopentene ("Selected Values of Properties of Hydrocarbons," API Project 44, Carnegie Institute of Technology, Pittsburgh, Pa.).

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Synthesis, Resolution, and Optical Rotatory Dispersion of a Hexa- and a Heptaheterohelicene

Sir:

Ever since Newman's synthesis and resolution of hexahelicene,¹ the optical properties of this system have fascinated chemists. As the archetype² of the inherently dissymmetric chromophore, its large rotation ($[\phi]_D^{20} 12,200^\circ$) coupled with its molecular simplicity ($C_{26}H_{16}$) has given fruitful stimulus to theoreticians.³ Its laborious synthesis^{1,2,4} coupled with a unique but

(1) (a) M. S. Newman, W. B. Lutz, and D. Lednicer, *J. Am. Chem. Soc.*, **77**, 3420 (1955); (b) M. S. Newman and D. Lednicer, *ibid.*, **78**, 4765 (1956).

(2) J. H. Brewster in "Topics in Stereochemistry," N. L. Allinger and E. Eliel, Ed., John Wiley & Sons, Inc., New York, N. Y., 1967, p 40.

(3) (a) D. D. Fitts and J. G. Kirkwood, *J. Am. Chem. Soc.*, **77**, 4940 (1955); (b) A. Moscovitz, *Tetrahedron*, **13**, 48 (1961); (c) I. Tinoco and R. W. Woody, *J. Chem. Phys.*, **40**, 160 (1964).

(4) M. S. Newman, R. S. Darlak, and L. Tsai, *J. Am. Chem. Soc.*, **89**, 6191 (1967).

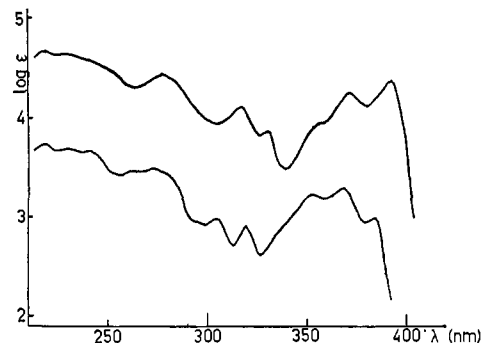


Figure 1. Uv spectra (cyclohexane) of IV and VIII. The spectrum of IV has been shifted downward over 1 log unit for the sake of clearness.

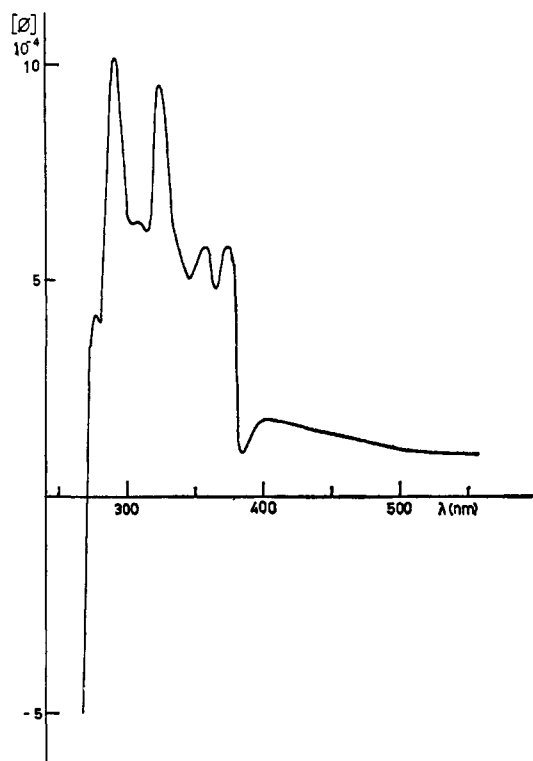


Figure 2. ORD spectrum of IV.

difficult resolution has limited extensive study of this fascinating ring system. The facile synthesis and high yield photocyclization of dithienylethenes to benzo-[1,2-*b*:4,3-*b'*]dithiophenes⁵ prompted us to attempt the preparation of some heterohelicenes.⁶ The hexaheterohelicene, benzo[*d*]naphtho[1,2-*d'*]benzo[1,2-*b*:4,3-*b'*]dithiophene (IV), and heptaheterohelicene, naphtho[1,2-*d*]benzo[*b'*]thieno[4,5-*d'*]benzo[1,2-*b*:4,3-*b'*]dithiophene (VIII), were prepared as shown in Scheme I. The synthesis of the two heterohelicenes proceeded in good yield and deserves little comment.⁷ Cyclization to IV was effected in 70% yield by irradiation of a

(5) R. M. Kellogg, M. B. Groen, and H. Wynberg, *J. Org. Chem.*, **32**, 3093 (1967).

(6) Similar ring closures furnishing benzohelicenes have recently been described: (a) M. Flammang-Barbieux, J. Nasielski, and R. H. Martin, *Tetrahedron Letters*, 743 (1967); (b) R. H. Martin, M. Flammang-Barbieux, J. P. Cosyn, and M. Gelbcke, *ibid.*, 3507 (1968).

(7) Correct analyses were obtained for all new compounds.

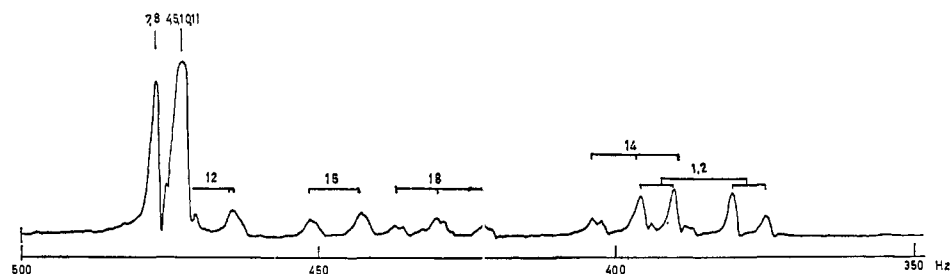
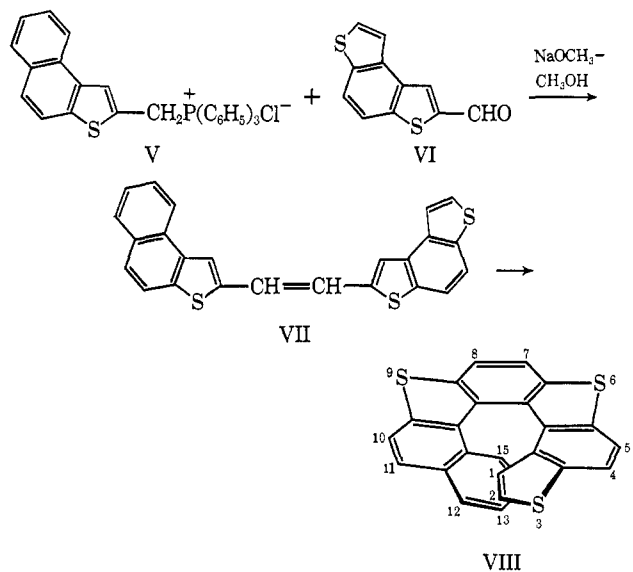
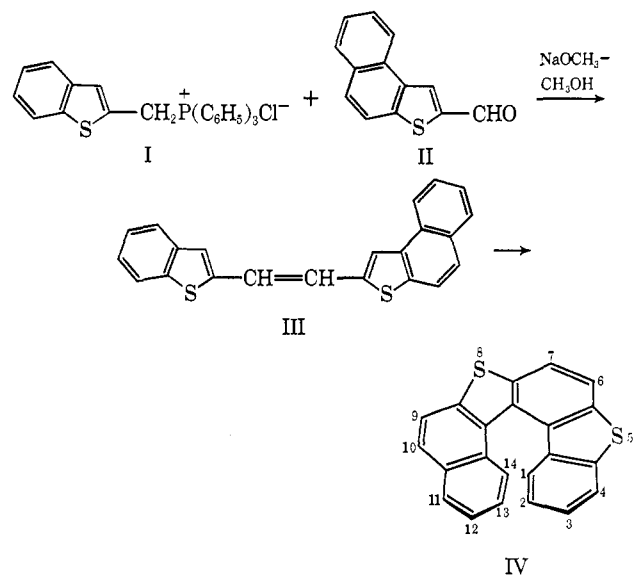


Figure 3. Nmr spectrum (60 Mc) of VIII (0.6% in CCl_4 ; CAT, 400 scans).

benzene solution containing a trace of iodine with a Hanau S 81 lamp. The hexaheterohelicene IV is a colorless compound, mp 223–225°. *Anal.* Calcd for

Scheme I



$\text{C}_{22}\text{H}_{12}\text{S}_2$: C, 77.6; H, 3.6; S, 18.8; mol wt, 340.5. Found: C, 77.3; H, 3.7; S, 18.8; mol wt, 340 (mass spectrometry). The uv spectrum is shown in Figure 1. Slow evaporation (standing overnight) of 100 mg of IV in 10 ml of benzene furnished crystals which were found to be optically active.⁸ The highest rotation observed was

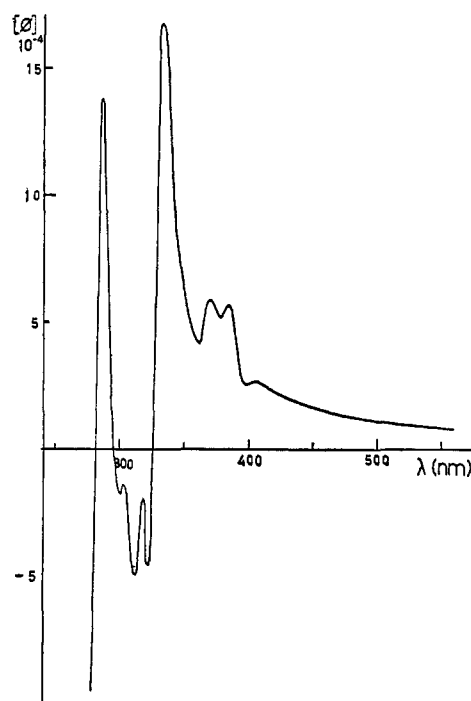


Figure 4. ORD spectrum of VIII.

$[\alpha]_{546}^{20} 2050^\circ$, $[\phi]_{290}^{20} 100,000^\circ$ (CHCl_3). The ORD spectrum is shown in Figure 2. Particularly noteworthy is the fact that IV racemized in solution with a half-life of 230 min at 22° (CHCl_3), whereas the crystals appeared to be optically stable. The ethylene VII, formed in 70% yield (exclusively *trans*), was cyclized as described, furnishing in 40% yield the pale yellow heptaheterohelicene VIII, mp 216–236°. ⁹ *Anal.* Calcd for $\text{C}_{24}\text{H}_{12}\text{S}_3$: C, 72.7; H, 3.1; S, 24.3; mol wt, 396.5. Found: C, 72.6; H, 3.1; S, 24.3; mol wt, 396 (mass spectrometry). The uv spectrum is shown in Figure 1 and the well-resolved and relatively simple nmr spectrum in Figure 3.

Resolution of VIII was achieved as described for VII, the highest rotation being $[\alpha]_{546}^{20} 2000^\circ$, $[\phi]_{332}^{20} 170,000^\circ$ (CHCl_3). The ORD spectrum is shown in Figure 4. The synthesis of heterohelicenes as described here has a number of advantages over that of the benzo analogs. The photocyclizations are unambiguous, in sharp contrast to those in the benzo series, in which isomeric phenanthrenes^{6b} and even anthracenes may

(8) This procedure was followed after reading details of the beautiful experiment described by Martin and coworkers.^{6b}

(9) The melting range of this analytically pure material probably indicates that partial resolution had taken place.

be formed.¹⁰ Moreover, heterohelicenes like VIII are useful as starting materials for higher members of the series since they allow selective substitution in the terminal heterocyclic ring.

(10) S. D. Cohen, M. V. Mijovic, and G. A. Newman, *Chem. Commun.*, 722 (1968).

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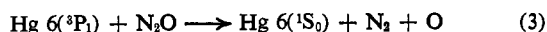
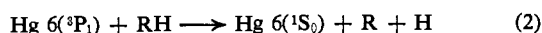
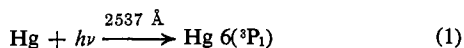
On the Inadequacy of the "Chemical Method" to Determine Relative Quenching Cross-Section Values for Mercury 6(³P₁) Atoms

Sir:

Quenching cross-section values (σ_Q^2) for Hg 6(³P₁) atoms, interacting with a large number of compounds, have been determined by a chemical method developed by Cvetanović.^{1,2} The results given below indicate that this method yields values for σ_Q^2 which are dependent upon the incident light intensity. The σ_Q^2 values for a given compound, as determined by the chemical method, will therefore depend upon the experimental conditions used. Thus the method will not provide a reliable σ_Q^2 value.

Values of I_a , the light absorbed per minute in the whole volume of the reaction cell, were determined by at least two different actinometries. The intensity of the incident light (I_{inc}) was calculated using the reaction cell surface which was exposed to the uv light.

Cvetanović,^{1,2} from 2537-Å irradiation of RH-nitrous oxide mixtures, in the presence of mercury, showed that the variation of the reciprocal of the quantum yield of the nitrogen product ($1/\varphi_{N_2}$) with the ratio of the concentrations, (RH)/(nitrous oxide), is linear. The observations have been explained by the following simplified mechanism.



This neglects the formation of Hg 6(³P₀) in the system. This mechanism has been used to relate the slope of the plot of $1/\varphi_{N_2}$ vs. (RH)/(N₂O) with the rate constant ratio k_2/k_3 .

$$\frac{1}{\varphi_{N_2}} = 1 + \frac{k_2(\text{RH})}{k_3(\text{N}_2\text{O})} \quad (6)$$

Figures 1 and 2 however show that for a change in I_{inc} of 10^3 , the slope of the straight line varies by a factor of 4.7 for *n*-butane and 1.3 for propylene. A variation in nitrogen quantum yield has also been reported for the diborane-nitrous oxide system.³ Since the slope depends on the value of I_{inc} , it is unlikely that it represents k_2/k_3 exclusively. The fact that the variation in the slope is de-

(1) R. J. Cvetanović, *J. Chem. Phys.*, **23**, 1208 (1955).

(2) R. J. Cvetanović, W. E. Falconer, and K. R. Jennings, *ibid.*, **35**, 1225 (1961).

(3) F. P. Fehlner and R. L. Strong, *J. Phys. Chem.*, **64**, 1522 (1960).

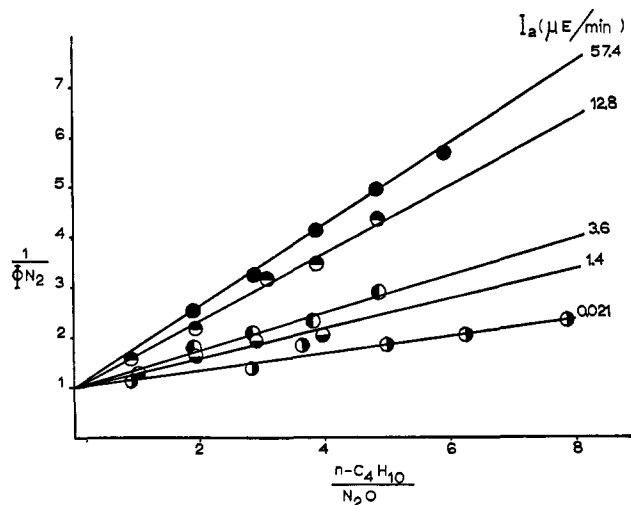


Figure 1. The variation of $1/\varphi_{N_2}$ with (*n*-butane)/(nitrous oxide) at different I_{inc} .

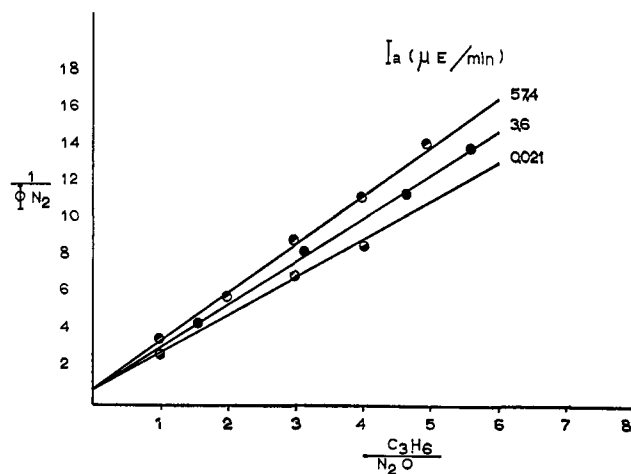


Figure 2. The variation of $1/\varphi_{N_2}$ with (propylene)/(nitrous oxide) at different I_{inc} .

pendent upon the compound used renders the "chemical method" unreliable for the determination of σ_Q^2 values.

The σ_Q^2 values, calculated using the equation

$$\frac{\sigma_1^2}{\sigma_2^2} = \frac{\beta_1(1 + M_{\text{Hg}}/M_2)^{1/2}}{\beta_2(1 + M_{\text{Hg}}/M_1)} \quad (7)$$

where σ^2 , β , and M represent the quenching cross-section value, the slope of the plot $1/\varphi_{N_2}$ vs. (RH)/(N₂O), and the atomic or molecular weight, respectively, and subscripts 1 and 2 refer to *n*-butane and propylene, respectively, are shown in Table I. The values indicate

Table I. Variation of the σ_Q^2 Values Calculated for Propylene with I_{inc}

I_{inc} , $\mu\text{Ein-cm}^{-2}$	I_a , $\mu\text{Ein-min}^{-1}$	β_1	β_2	σ_1^2 , \AA^2	σ_2^2 , \AA^2
1.12	57.4	0.80	2.8	3.6 ^a	11.1
0.65	12.8	0.67
0.18	3.6	0.37	2.5	...	21.4
0.071	1.4	0.29
0.0011	0.021	0.17	2.2	...	40.8

^a Reference standard.