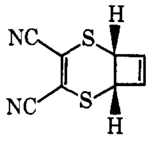
Table I. Reaction Conditions, Products, and Yields

Precursor	200°[a]	400°[b]	$h\nu$[c]
4	Tar	Phthalonitrile (61%) and sulfur (trace)	Phthalonitrile (30%) and sulfur 15%)
5	**7** (11%) and starting material (59%)	Naphthalene (30%), thiophene (5%), sulfur (3%), and four unidentified products	**8** (5%), starting material (50%), and one unidentified product
6	Benzene (50%) and starting material (50%)[d]	Benzene (27%), thiophene (trace), sulfur (13%), and phenyl disulfide (2%)	*e*

[a] In glass tubes sealed under vacuum. [b] In quartz tube packed with quartz wool at 0.05 mm pressure. [c] Dioxane solutions irradiated for 24 hr with a GE Sunlamp at 50°. [d] After 1 hr, nmr analysis. [e] Irradiation for 5 hr produced a mixture of polymer and unreacted **6**.

(CCl_4) δ 4.50 and 5.78 (2 H, m, $W_{1/2} \simeq 2$ Hz) and 7.21 ppm (AA'BB' m); and mass spectrum m/e 147 and 192 (M^+)], and **6** [32%; mp 49–52°; nmr (CCl_4) δ 4.42, 5.86, and 6.70 ppm (2 H, m, $W_{1/2} \simeq 2$ Hz); and mass spectrum m/e 97 and 142 (M^+)].



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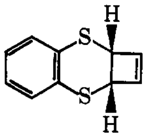

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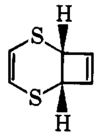
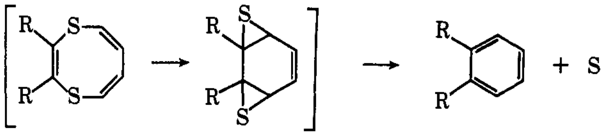


6

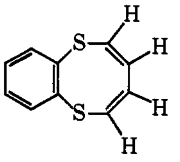
The production of 1,4-dithiocins from **4**, **5**, and **6** requires disrotation if the ring openings are to be synchronous processes. Stepwise processes are highly tenable, however, in view of the stabilizing influences available to radical intermediates. Accordingly, both the photolytic and thermal behavior of these substances were examined. The results are presented in Table I.

The most prominent chemical feature of compounds **4**, **5**, and **6** is their propensity to lose sulfur giving benzenoid aromatics. This reaction pathway is formulated as follows



Ring opening to the 1,4-dithiocin is followed by spontaneous valence isomerization (an internal Diels–Alder reaction) leading to bisepisulfides. These can lose sulfur either thermally[14] or photochemically.[15]

Facile desulfurization leading to benzenoid aromatics is a salient feature in the chemistry of thiepines[16] and has been formulated in terms of an episulfide intermediate for that system also.[17] Thiepines neither show nor are expected[18] to show aromatic character. The formation of phthalonitrile, naphthalene, and benzene from compounds **4**, **5**, and **6**, respectively, therefore suggests that there is no significant aromatic stabilization of the corresponding 1,4-dithiocins.



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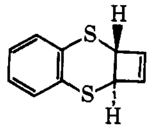

8

Under the milder of the two pyrolysis conditions examined (lower temperatures effected no change), compound **5** is partially converted to 1,6-benzodithiocin (**7**). This product was isolated as a yellow oil by preparative tlc and further purified by vacuum distillation (oven temperature 130° (0.05 mm)). Its nmr spectrum consists of two AA'BB' multiplets of equal areas centered at 6.23 and 7.25 ppm. The signal at 6.23 ppm precludes the presence of a diamagnetic ring current in the heterocyclic ring. Other spectral properties of this compound include: ir (film) bands at 1565, 1600, 2850, 2920, 2950, 2990, 3010, and 3025 cm^{-1}; uv max (cyclohexane) 235 (10,500), 252 (10,800), 278 (3480), and 355 (825); and mass spectrum m/e 147 (100%) and 192 (37%, M^+).

Irradiation of compound **7** (sunlamp, cyclohexane, 2 hr) effects quantitative conversion back to compound **5**. Vacuum pyrolysis (quartz tube at 400°) produces naphthalene as expected.

Photolysis of compound **5** produced in low yield a crystalline substance (mp 84–87°) with nmr and mass spectra quite similar to those of **5** itself. This material is accordingly formulated as the trans isomer **8**. The nmr spectrum shows, in addition to the AA'BB' multiplet centered at 6.96 ppm, two 2 H quartets at 4.28 and 6.48 ppm ($J = 1.2$ Hz) indicating that the vicinal and allylic coupling constants must be nearly equal in this isomer.

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[14] B. P. Stark and A. J. Duke, "Extrusion Reactions," Pergamon Press, New York, N. Y., 1957, p 93.

[15] Several examples are listed by E. Block, *Quart. Rep. Sulfur Chem.*, 4, 237 (1969).

[16] G. P. Scott, *J. Amer. Chem. Soc.*, **75**, 6332 (1953); K. Dimroth and G. Lenke, *Chem. Ber.*, **89**, 2608 (1956); J. D. Loudon and A. D. B. Sloan, *J. Chem. Soc.*, 3262 (1962); V. J. Traynelis and J. R. Livingston, *J. Org. Chem.*, **29**, 1092 (1964); W. E. Parham and D. G. Weetman, *ibid.*, **34**, 56 (1969); H. Hofmann, H. Westernacher, and H. Haberstroh, *Chem. Ber.*, **102**, 2595 (1969).

[17] R. Grigg, R. Hayes, and J. L. Jackson, *Chem. Commun.*, 1167 (1969).

[18] M. J. S. Dewar and N. Trinajstic, *J. Amer. Chem. Soc.*, **92**, 1453 (1970).

Crystal Structure and Spectroscopic Properties of the 1-Azabicyclo[3.3.3]undecane System

Sir:

Bicyclo[3.3.3]undecane (**1**)[1,2] and 1-azabicyclo[3.3.3]undecane (**2**),[2] prototypes containing three eight-

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[1] M. Doyle, W. Parker, P. A. Gunn, J. Martin, and D. D. MacNicol, *Tetrahedron Lett.*, 3619 (1970).

[2] N. J. Leonard and J. C. Coll, *J. Amer. Chem. Soc.*, **92**, 6685 (1970); **93**, 287 (1971).

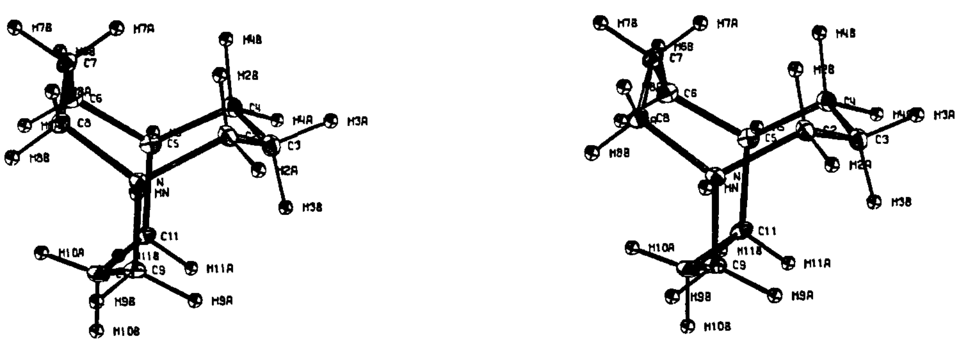
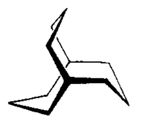


Figure 1. Stereoscopic view of the cation of 1-azabicyclo[3.3.3]undecane hydrochloride (3) looking nearly along the N(1)-C(5) axis.

membered rings,[3] have recently been synthesized, and favored BC-BC-BC (boat-chair) conformations were postulated. We now present the results of the X-ray crystallographic examination of the hydrochloride salt of **2**, which confirm these ring conformations and which indicate, along with some unusual spectroscopic properties, the presence of internal strain.

Crystal data for 1-azabicyclo[3.3.3]undecane hydrochloride (**3**)[2] are: $C_{10}H_{20}NCl$, mol wt = 189.7; triclinic, a = 10.830 (8), b = 7.122 (6), c = 7.014 (3) Å, $\alpha = 97° 58' (4')$, $\beta = 90° 24' (4')$, $\gamma = 96° 17' (4')$, V = 532.4 Å^3, ρ_{measd} = 1.24 g cm^{-3}, Z = 2, ρ_{calcd} = 1.18 g cm^{-3}; space group $P\bar{1}$. Intensity data were collected on a Picker FACS-1 computer-controlled diffractometer (Cu Kα radiation). The structure (Figure 1) has been refined by full-matrix least-squares methods to R = 0.047 on 1664 nonzero reflections.

The cation of **3** possesses effective but noncrystallographic C_3 symmetry with each of the three constituent eight-membered rings in the BC conformation. The crystal structure consists of individual rows containing an essentially linear arrangement of alternating cations and hydrogen-bonded chloride anions, with adjacent rows containing all R or all S cations. The nmr spectra of the hydrochloride **3** at 60, 100, and 220 MHz show the signal for the bridgehead methine proton as a septet (J = 5 Hz), suggesting rapid inversion of conformation, making the vicinal (C-2,8,9) methylene protons equivalent. In the 100-MHz spectrum of **3** we were unable to obtain convincing evidence of conformational immobilization[4] in the range +95 to −150° while trying a variety of solvents; however, a "frozen" spectrum of the free base was obtained at *ca.* −80°, corresponding to slowed inversion of conformations (configurations).[5]



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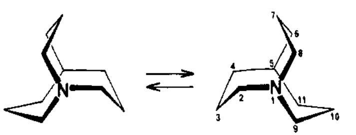

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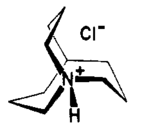

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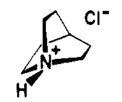

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The presence of internal strain in **3** is evident from the angles[6] obtained by X-ray analysis: HN^+-CH_2-CH_2, 117.0-117.4 (3)°; CH_2-CH_2-CH_2, 119.5-120.1 (2)°; CH_2-CH_2-CH(methine), 117.4-118.7 (3)°. The C-N lengths range from 1.511 to 1.519 (4); C(methylene)-C(methylene), 1.497-1.522 (5); and C(methylene)-C(methine), 1.535-1.549 (5) Å. The principal difference between the structure (Figure 1) found in this study and that represented by Dreiding or Fieser models of **3** involves a pushing apart of the endo hydrogen atom on C-7 from the intraannular[7] hydrogens on C-2 and C-4.[8] By this action, the torsion angles in the trimethylene bridges, which appear slightly greater than 90° in the model, are reduced to the observed 66.5-68.7°, thus providing some energy compensation.[9]

Comparison of the bicyclo[3.3.3]undecane system with the bicyclo[2.2.2]octane system is especially interesting since, by contrast, the bond angles in the latter are close to tetrahedral.[10] 1-Azabicyclo[3.3.3]undecane hydrochloride (**3**) is a stronger conjugate acid than quinuclidine hydrochloride (**5**), *i.e.*, pK_a' 8.8 *vs.* 10.05 in 66% DMF and ~9.9 *vs.* ~10.9 in water,[11] respectively. The greater acidity of **3** can be accounted for by relatively greater p character of the $^+$N-H due to the flattening at the bridgehead nitrogen (CH_2-$^+$NH-CH_2

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[3] The name "manxane" has been suggested for **1**[1] inspired by the coat of arms of the Isle of Man. On the same basis, we feel that **2** qualifies for the name "manxine."

[4] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959, Chapter 10.

[5] This result closely parallels the observed behavior of the hydrocarbon **1** at −80° using 100 MHz.[1] Hence, an alternative conformational change of **2** involving inversion of nitrogen and equilibrium with the (from models) much less favored "nitrogen-in" conformation [H. E. Simmons and C. H. Park, *J. Amer. Chem. Soc.*, **90**, 2428 (1968)] has not been considered important for the [3.3.3] case.

[6] See J. D. Dunitz in "Perspectives in Structural Chemistry," Vol. II, J. D. Dunitz and J. A. Ibers, Ed., Wiley, New York, N. Y., 1968, pp 35-39.

[7] M. Bixon, H. Dekker, J. D. Dunitz, H. Eser, S. Lifson, C. Mosselman, J. Sicher, and M. Svoboda, *Chem. Commun.*, 360 (1967).

[8] The various intraannular 1,4 H-H distances (*e.g.*, H-2b-H-7a in **3**) range from 2.12 (5) to 2.28 (5) Å and the intraannular 1,3 H-H distances (*e.g.*, H-2b-H-4b) from 2.67 (5) to 2.78 (5) Å, compared with 2.4 Å for twice the van der Waals radius of hydrogen [L. Pauling in "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960, pp 257-264]. These H-H distances should not be greatly affected (and if anything, decreased) by the tendency for hydrogen atoms to be positioned too near the attached carbon atom in an X-ray study.

[9] *Cf.* 65 and 67° for the corresponding torsion angles in cyclooctane-*cis*-1,2-dicarboxylic acid [H. B. Bürgi and J. D. Dunitz, *Helv. Chim. Acta*, **51**, 1514 (1968)]; see also I. C. Paul and K. T. Go, *J. Chem. Soc. B*, 33 (1969); S. M. Johnson, C. A. Maier, and I. C. Paul, *ibid.*, *B*, 1603 (1970).

[10] See O. Ermer and J. D. Dunitz, *Chem. Commun.*, 567 (1968); O. Ermer and J. D. Dunitz, *Helv. Chim. Acta*, **52**, 1861 (1969); A. F. Cameron, G. Ferguson, and D. G. Morris, *J. Chem. Soc. B*, 1249 (1968); A. Meyerhöffer and D. Carlström, *Acta Crystallogr., Sect. B*, **25**, 1119 (1969).

[11] We are grateful to Mr. George Maciak, Eli Lilly and Co., for these determinations.

angles 115.0–115.9 (2)°), together with possibly greater F strain[12] in **3** than in **5**. The bridgehead carbon (C-5) of **3** is also flattened (CH_2–CH–CH_2 angles, 113.5–114.8 (3)°), leading to greater p character in the C(methine)–H bond.[13] This is corroborated by the coupling, $J_{^{13}C-H}$,[14] of the methine carbon and proton which was estimated as 121 ± 5 Hz for the hydrochloride **3**, compared with the $J \geqslant 140$ Hz observed for the bridgehead ^{13}C–H in quinuclidine hydrochloride. Both the ^{13}C nmr[15] and the ^1H nmr spectra indicated the unusual nature of the methine carbon and proton. Thus, the chemical shift for C-5 in the [3.3.3]amine hydrochloride (**3**) is at *lower field* (869 Hz upfield from dioxane) than the β_N carbons (915 Hz), whereas in quinuclidine hydrochloride (**5**) C-4 is at higher field (1083 Hz) than the β_N carbons (1000 Hz). The chemical shift for H-5 (δ 2.57 in $CDCl_3$–TMS) in the [3.3.3]-amine **2** is at lower field than the β_N CH_2's (δ 1.60), and this is also true for its hydrochloride **3** (δ 2.60 *vs.* 1.93), whereas H-4 in quinuclidine (**4**) (1.3–1.8) is in the same range as the β_N CH_2's (1.50) in that molecule.

The uv maximum for **2** is at an exceptionally long wavelength (240 nm, ϵ 2935 in ether!) for a saturated tertiary amine;[16] by contrast, quinuclidine (**4**) in diethyl ether solution shows only end absorption (above 200 nm). The spectrum of "manxine" (**2**) vapor exhibits extensive fine structure in the range 280–205 nm, with major absorption in the region 260–230 nm, at longer wavelength than that of quinuclidine in the vapor state.[17] The ultraviolet absorption of the amine **2** thus reflects the reduction in energy difference for the n → p transition between the ground state, where we observe a flattening of the nitrogen bridgehead in **3**, and the excited state, where, by analogy to quinuclidine (**4**), the nitrogen is expected to approach coplanar bonding.[17]

Acknowledgment. The authors are indebted to the National Science Foundation for financial support (Research Grant No. GP-8407X) and for assistance in the purchase of the 220-MHz spectrometer used in this work.[18]

[12] H. C. Brown, D. H. McDaniel, and O. Häfliger in "Determination of Organic Structures by Physical Methods," Vol. 1, E. A. Braude and F. C. Nachod, Ed., Academic Press, New York, N. Y., 1955, Chapter 14. See in Figure 1 the interaction of H2A, H8A, and H9A with HN.

[13] See M. J. Sabacky, S. M. Johnson, J. C. Martin, and I. C. Paul, *J. Amer. Chem. Soc.*, **91**, 7542 (1969).

[14] For theoretical considerations, see N. Muller and D. E. Pritchard, *J. Chem. Phys.*, **31**, 768, 1471 (1959); K. Mislow, *Tetrahedron Lett.*, 1415 (1964); C. S. Foote, *ibid.*, 579 (1963).

[15] (a) ^{13}C spectra courtesy of Brucker Scientific, Inc., Elmsford, N. Y. (b) We also thank J. Jonas, R. L. Thrift, and J. R. Lombardi for very helpful discussions during this investigation.

[16] N. J. Leonard and D. M. Locke, *J. Amer. Chem. Soc.*, 77, 437 (1955).

[17] A. M. Halpern, J. L. Roebber, and K. Weiss, *J. Chem. Phys.*, **49**, 1348 (1968).

[18] The X-ray structure analysis here reported was carried out as part of formal X-ray lecture and laboratory courses in crystal structure analysis given at the University of Illinois in the fall in 1970. We acknowledge the participation, interest, and enthusiasm of Carolyn I. Hejna, Alice C-Z. Shen, John Vandervoorn, Jr., and Stephen R. Byrn.

[19] Alfred P. Sloan Research Fellow, 1968–1970.

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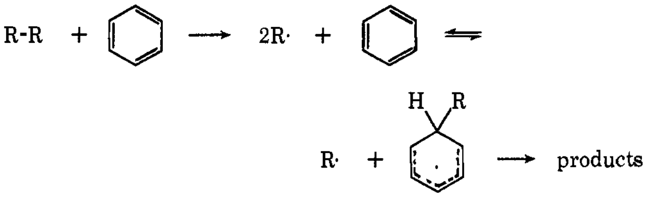
Chemically Induced Dynamic Nuclear Polarization and Substituent Effects in Some Homolytic Aromatic Substitution Reactions

Sir:

In homolytic aromatic substitution reactions any substituents in the substrate activate the ortho and para positions toward the attack of electrically neutral, free radicals.[1] However, upon investigating the corresponding reactions of the free radicals (R·) obtained by pyrolysis of bis(pentafluorobenzoyl) peroxide[2] (R–R) with the chemically induced dynamic nuclear polarization (CIDNP) method,[3] we found the substituent effects of *electrophilic* aromatic substitution.

In a typical experiment a 0.75 *M* solution of R–R in hexachlorobutadiene is decomposed in the presence of 1 *M* benzene at 160° in a 60-MHz nmr spectrometer. One observes the benzene resonance in emission, and other emission (E) and enhanced absorption (A) lines, attributed to the products pentafluorobenzoic acid (I), substituted 1,3- and 1,4-cyclohexadienes (II), and pentafluorobenzoates (III).

We assume that R· adds reversibly to benzene[4] to form 1-substituted cyclohexadienyl radicals (IV) still in the primary cage.[5] The resulting singlet radical pairs, R· + IV, can either react to afford the products I–III, or change their multiplicity to yield triplet pairs. The triplet pairs will separate and preferably cleave to the reactants, *i.e.*, benzene and R·.



IV

Because the rates of multiplicity change are nuclear spin dependent,[6] CIDNP is expected for both the

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[1] G. H. Williams, "Homolytic Aromatic Substitution," Pergamon Press, London, 1960.

[2] M. W. Buxton, British Patent 977,963 (1964).

[3] J. Bargon, H. Fischer, and U. Johnsen, *Z. Naturforsch. A*, **22**, 1551 (1967); H. Fischer and J. Bargon, *Accounts Chem. Res.*, **2**, 110 (1969).

[4] From product studies, ^{19}F-CIDNP, and esr results we conclude tentatively that R· = pentafluorobenzoate. The role of pentafluorophenyl radicals is being further investigated. For other reversible additions to benzene see: T. Nakata, T. Tokumaru, and O. Simamura, *Tetrahedron Lett.*, 3303 (1967); O. Volkert and D. Schulte-Frohlinde, *ibid.*, 2151 (1968); M. L. Poutsma in "Methods of Free Radical Chemistry," E. S. Huyser, Ed., Vol. 1, Marcel Dekker, New York, N. Y., 1969, p 32, and references therein; J. Saltiel and H. C. Curtis, *J. Amer. Chem. Soc.*, **93**, 2056 (1971).

[5] The lifetime of the primary cage is considered to be 10^{-10}–10^{-9} sec [*cf.* L. Herk, M. Feld, and M. Szwarc, *ibid.*, **83**, 2998 (1961)]. Therefore, R· must add to benzenes with a rate constant on the order of 10^7–10^8 M^{-1} sec^{-1}. Consistently, addition rates of 10^9 M^{-1} sec^{-1} have been measured for hydroxyl and hydrogen radicals to benzenes and pyridines [*cf.* P. Neta and L. M. Dorfman, *J. Chem. Phys.*, **73**, 413 (1969); *Advan. Chem. Ser.*, **No. 82**, 222 (1968); B. Cercek and M. Ebert, *Trans. Faraday Soc.*, 1687 (1967)]. However, De Tar has estimated the unknown addition rate of benzoyloxy radicals to benzenes to be 35 M^{-1} sec^{-1} [D. F. De Tar, *J. Amer. Chem. Soc.*, **89**, 4058 (1967)] in which case spin correlation is lost. The fast reaction of pentafluorobenzoyloxy radicals with benzenes could be due to a π complex formation between the peroxide and the aromatic substrates which would provide a benzene molecule in the immediate vicinity when the radical pair is generated. Another case of spin-correlation conservation has been observed by R. Kaptein, *et al.*, during reactions of isobutyryl peroxide with $CBrCl_3$ (R. Kaptein, F. W. Verheus, and L. J. Oosterhoff in R. Kaptein, Thesis, University of Leiden, The Netherlands, 1971, p 41).

[6] (a) G. L. Closs, *J. Amer. Chem. Soc.*, **91**, 4552 (1969); G. L. Closs and A. D. Trifunac, *ibid.*, **91**, 4554 (1969); **92**, 2183, 2186 (1970);