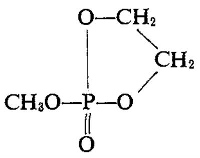
as $SbCl_5$ at room temperature and above (where most kinetic processes have been studied) lies in the range 10^2 to 10^8 sec^{-1}. It seems altogether reasonable then that, in some mechanistic studies, pseudorotations of trigonal-bipyramidal intermediates must be considered in accounting for product distribution. The main requirement exists that the lifetime of the intermediate exceeds the exchange time.

In fact, in the hydrolysis of cyclic phosphate esters, for example



Dennis and Westheimer[20] postulate a pseudorotation of the trigonal-bipyramidal intermediate to account for the products formed. In their case, relatively light atoms are involved, and the reaction rate, ~10^{-4} sec^{-1} (mol/l.)$^{-1}$ at room temperature, is slow enough for exchange to occur.

However, it is clear that for the molecules under consideration pseudorotation is possible only because the coordinate governing exchange has a low frequency and large amplitude motion (hence a correspondingly small force constant) associated with a molecule of comparatively low reduced mass. The latter conditions may apply for these trigonal-bipyramidal molecules because of the apparent weakness of axial bonds compared to equatorial bonds.

[20] E. A. Dennis and F. H. Westheimer, *J. Amer. Chem. Soc.*, **88**, 3432 (1966).

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The Molecular Geometry of Derivatives of 1H-Azepine in the Free and Complexed State[1]

Sir:

The 1H-azepine molecule (**1a**) is isoelectronic with the cycloheptatrienide anion[2] and, if planar, may in actuality be antiaromatic.[3] Interestingly, molecular quantum mechanical calculations for such a model predict marked polyenic character and strong localization of the π electrons on nitrogen and the double bonds of the seven-membered ring with little, if any, tendency for delocalization.[4] Although the parent 1H-azepine (**1a**) remains to be synthesized, a few derivatives have been known since 1963.[5,6] To the present time, however, no X-ray structural information has been obtained on these nitrogen-containing eight-π-electron systems. In an effort to elucidate the molecular geometry of this seven-membered ring in the free state, and when complexed with iron tricarbonyl,[7] we have carried out three-dimensional X-ray studies on **1b**[8] and on the $Fe(CO)_3$ complex of **1c**.[8]

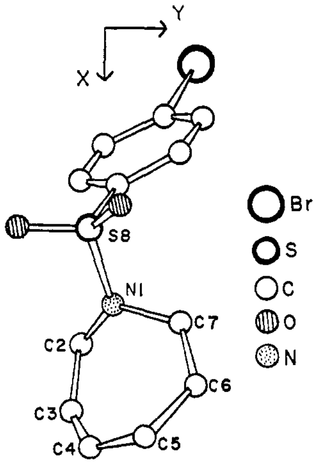
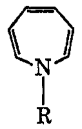


Figure 1. A view of **1b** looking along the *z* axis. Important distances are N_1–C_2 1.43 Å, C_2–C_3 1.38 Å, C_3–C_4 1.44 Å, C_4–C_5 1.34 Å, C_5–C_6 1.46 Å, C_6–C_7 1.37 Å, N_1–C_7 1.45 Å, and N_1–S_8 1.61 Å (estimated standard deviation ±0.02 Å). The angles within the seven-membered ring are N_1 116°, C_2 118°, C_3 127°, C_4 123°, C_5 127°, C_6 124°, and C_7 121° (estimated standard deviation ±1.5°). The $S_8N_1C_2$ and $S_8N_1C_7$ angles are 118 and 120°, respectively.



1a, R = H
b, R = $SO_2C_6H_4Br$-*p*
c, R = $COOCH_3$

1b crystallizes as lemon-yellow prisms, generally elongated along the *b* axis, and belongs to the orthorhombic system, with $a = 12.32$, $b = 5.96$, and $c = 16.53$ Å (Mo Kα, λ 0.7107 Å). There are four molecules of $C_{12}H_{10}BrNO_2S$ (mol wt 312.2) in the unit cell ($\rho_{meas} = 1.68$ g cm^{-3}; $\rho_{calcd} = 1.71$ g cm^{-3}). Systematic absences establish the space group as $P2_12_12_1$. The structure was determined by the heavy-atom method and has been refined by full-matrix least squares on 1274 independent intensities collected photographically (Cu Kα radiation) to an *R* factor of 0.10. A view of the structure with important molecular dimensions is given in Figure 1.

The iron tricarbonyl complex of **1c** crystallizes as irregular orange prisms belonging to the triclinic system, with $a = 8.62$, $b = 6.47$, and $c = 10.90$ Å; $\alpha = 93.4°$, $\beta = 93.0°$, and $\gamma = 104.4°$ (Mo Kα, λ 0.7107 Å). There are two molecules of $C_8H_9NO_2 \cdot Fe(CO)_3$ (mol wt 291.0) in the unit cell ($\rho_{meas} = 1.60$ g cm^{-3}; $\rho_{calcd} = 1.65$ g cm^{-3}), and the structural analysis indicates that the space group is $P\bar{1}$. The structure has been refined by full-matrix least squares on 2008 independent intensities collected photographically (Mo Kα radiation) to an *R* factor of 0.10. A view of the structure is shown in Figure 2.

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[1] Paper XLVI in the unsaturated heterocyclic systems series from The Ohio State University laboratories.

[2] L. A. Paquette and J. H. Barrett, *J. Am. Chem. Soc.*, **88**, 1718 (1966).

[3] R. Breslow, J. Brown, and J. J. Gajewski, *ibid.*, **89**, 4383 (1967).

[4] R. W. Schmid, *Helv. Chim. Acta*, **45**, 1982 (1962).

[5] (a) K. Hafner and C. König, *Angew. Chem.*, **75**, 89 (1963); (b) W. Lwowski, T. J. Maricich, and T. W. Mattingly, Jr., *J. Am. Chem. Soc.*, **85**, 1200 (1963); (c) R. J. Cotter and W. F. Beach, *J. Org. Chem.*, **29**, 751 (1964).

[6] For details of the preparation of substituted 1H-azepines, see L. A. Paquette and D. E. Kuhla, *Tetrahedron Letters*, 4517 (1967).

[7] E. O. Fischer and H. Rühle, *Z. Anorg. Allgem. Chem.*, **341**, 137 (1965).

[8] The synthesis of this material will be published independently.

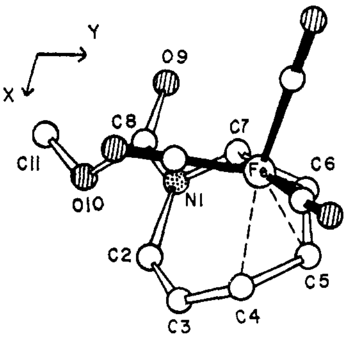


Figure 2. A view of the iron tricarbonyl complex of **1c** viewed along the *z* axis; the carbonyl groups are shaded in black. Within the seven-membered ring the distances are N_1–C_2 1.38 Å, C_2–C_3 1.34 Å, C_3–C_4 1.45 Å, C_4–C_5 1.40 Å, C_5–C_6 1.41 Å, C_6–C_7 1.43 Å, N_1–C_7 1.43 Å, and N_1–C_8 1.37 Å (estimated standard deviation ±0.010–0.015 Å). The angles within the ring are N_1 124°, C_2 123°, C_3 129°, C_4 126°, C_5 118°, C_6 120°, C_7 125° (estimated standard deviation ±1°). The $C_8N_1C_2$ and $C_8N_1C_7$ angles are 120 and 116°, respectively.

In **1b**, the molecule exists in a "boat" conformation[9] relative to the best plane (maximum deviation 0.02 Å) through the atoms C_2, C_3, C_6, and C_7, with N_1, C_4, and C_5 lying 0.60, 0.58, and 0.54 Å, respectively, from this plane. The double bonds are definitely localized at C_2–C_3, C_4–C_5, and C_6–C_7, in contrast to the situation observed in tropolone in both anionic and cationic forms[10,11] and in 2-chlorotropone,[12] although bond alternation has been recognized in cupric tropolone.[13] The two atoms comprising each double bond and their immediate neighbors are coplanar (maximum deviation 0.01 Å). The dihedral angles within the seven-membered ring are listed in Table I. N_1 deviates by 0.22 Å from the plane defined by C_2, C_7, and S_8. This is a relatively small deviation for sp^3 hybridization and, together with the valency angles around N_1, implies substantial sp^2 character for the nitrogen atom. The dimensions of the benzenesulfonyl group attached to nitrogen are similar to those reported recently in sulfaguanidine monohydrate.[14]

Table I. Dihedral Angles in the Azepine Ring in the Free State and When Complexed with Iron Tricarbonyl[a]

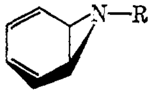
ABCD	**1b**	Fe(CO)₃ of— **1c**	Fe(CO)₃ of— Tropone
$C_7N_1(C_1)C_2C_3$	64	0	22
$N_1(C_1)C_2C_3C_4$	−3	−5	−7
$C_2C_3C_4C_5$	−34	−45	−48
$C_3C_4C_5C_6$	1	48	53
$C_4C_5C_6C_7$	35	2	5
$C_5C_6C_7N_1(C_1)$	−2	−71	−49
$C_6C_7N_1(C_1)C_2$	−61	54	23
$C_6C_7N_1(C_1)X$	147	−128	−162
$XN_1(C_1)C_2C_3$	−143	−178	−152
Atom 1	N	N	C
Atom X	S	C_8	O

[a] The angles calculated from the coordinates in troponeiron tricarbonyl are listed for comparison.[b] The angle ABCD is considered positive if, when looking along the BC bond from B to C, atom A has to be rotated clockwise to eclipse atom D. [b] In troponeiron tricarbonyl, the atom numbering has been changed from that given in the original publication[c] so that the ring consists of C_1–C_7, the carbon of the carbonyl group is C_1, and the $Fe(CO)_3$ group complexes to C_4, C_5, C_6, and C_7. [c] R. P. Dodge, *J. Am. Chem. Soc.*, **86**, 5429 (1964).

The iron tricarbonyl moiety complexes to a four-carbon atom residue *cis* to the carbonyl group in **1c**.[15] The Fe-complexing carbon atom distances range from 2.05 to 2.15 Å, and, as the Fe–N_1 and Fe–C_3 distances are effectively equal (3.08 and 3.06 Å), it does not appear that nitrogen participates in the complex formation. The two groups of four atoms C_4, C_5, C_6, and C_7 and N_1, C_2, C_3, and C_4 are approximately planar (maximum deviation 0.01 Å), with C_7, C_8, O_9, O_{10}, and C_{11} all within 0.06 Å of the latter plane; the dihedral angle between these planes is 133°. The bond distances C_4–C_5, C_5–C_6, and C_6–C_7 are effectively equal and are consistent with delocalization in this portion of the seven-membered ring,[16] while C_2–C_3 is a localized double bond. N_1 is 0.01 Å from the plane defined by its three-bonded neighbors.

The terminal atoms of the "butadiene group" each deviate by 0.05 Å from the plane defined by the other three atoms. The geometry of this complex bears a general resemblance to the $Fe(CO)_3$ complexes of 2,4,6-triphenyltropone[17] and of tropone,[18] the most significant difference being the greater tendency toward planarity at N_1 in the present structure.[19] The angles C(carbonyl)–Fe–C(carbonyl) can be divided into two large (99.5 and 101.6°) and one small (90.7°) as is generally true in $Fe(CO)_3$-conjugated diolefin complexes.[20]

The present study reveals that **1b** and, therefore, presumably all closely related 1H-azepines, exhibit little propensity to exist in the azanorcaradiene tautomeric form (**2**) or as azahomoaromatic entities of type **3**, but are true polyenes.



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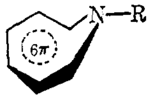

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[9] E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Publishers, New York, N. Y., 1965, pp 206–209.

[10] Y. Sasada and I. Nitta, *Acta Cryst.*, **9**, 205 (1956); R. Shiono, *ibid.*, **14**, 42 (1961).

[11] Y. Sasada and I. Nitta, *Bull. Chem. Soc. Japan*, **30**, 62 (1957).

[12] E. J. Forbes, M. J. Gregory, T. A. Hamor, and D. J. Watkin, *Chem. Commun.*, 114 (1966).

[13] W. M. Macintyre, J. M. Robertson, and R. F. Zahrobsky, *Proc. Roy. Soc.* (London), **A289**, 161 (1966).

[14] M. Alleaume, Abstracts of the American Crystallographic Association Winter Meeting, Tucson, Ariz., 1968, p 16, paper B6.

[15] H. Günther and R. Wenzl, *Tetrahedron Letters*, 4155 (1967).

[16] The question of localized or delocalized π electrons in the "butadiene" portion of the ligand and its relation to a π- or σ–π bond picture has been recently discussed by M. R. Churchill and R. Mason, *Advan. Organometal. Chem.*, **5**, 93 (1967), and by R. Pettit and G. F. Emerson, *ibid.*, **1**, 1 (1964).

[17] D. L. Smith and L. F. Dahl, *J. Am. Chem. Soc.*, **84**, 1743 (1962).

[18] See Table I, footnote *c*.

[19] A referee has suggested that the apparently shorter N_1–C_2 distance in the complex of **1c**, when compared to N_1–C_7 in that structure and to N_1–C_2 and N_1–C_7 in **1b**, may imply some interaction between N_1 and the C_2–C_8 double bond in the complex of **1c**. Such an effect would contribute to the planarity at N_1 and would be more likely in a urethan than in a simple amide or a sulfonamide.

[20] See, for example, O. S. Mills and G. Robinson, *Acta Cryst.*, **16**, 758 (1963); B. Dickens and W. N. Lipscomb, *J. Chem. Phys.*, **37**, 2084 (1962).

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