Electron Spin Resonance Study of Some Iminoxy Radicals. Stereochemistry of Bicyclic Systems

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Abstract: The iminoxy radicals obtained from some substituted bicyclic oximes (I-XX) have been studied by esr spectroscopy. On the basis of molecular geometry dependence of hfs constants, the conformational effects of the 2 and 2,4 substitution on the frameworks of bicyclo[3.3.1]nonane, bicyclo[3.3.1]nonene, and bicyclo[3.2.1]octane systems have been investigated. The introduction of a bulky substituent (*e.g.*, morpholinyl, phenyl) in the exo-2 or exo,exo-2,4 positions in the bicyclo[3.3.1]nonane system (sp^2 hybridization at C-9) leads to a preferred chair-boat conformation for this framework, unlike the effect of the same substituents in the endo-2- (or endo,endo-2,4-) or endo,exo-2,4 positions which preserves the chair-chair conformation for this framework.

I n the attempt to correlate hfs constants with the molecular geometry and the calculated spin densities, a great number of iminoxy radicals obtained from bicyclic compounds[2] were studied by esr. Although some theoretical studies[3] have been undertaken to rationalize the hfs obtained in the iminoxy radicals in terms of calculated spin densities, a simple way (as McConnell-type relationship[4] is for π radicals) relating the two quantities has not been found. However, information particularly useful on the configuration and conformation of bicyclic compounds can be extracted from the esr experimental data of the iminoxy radicals.

This work completes and extends our previous works[2c,d] on the stereochemistry of some substituted bicyclo[3.3.1]nonane, bicyclo[3.3.1]nonene, and bicyclo[3.2.1]octane systems, studied as iminoxy radicals.

Results and Discussion

The investigated oximes were derivatives of bicyclo-[3.3.1]nonane (I-XI), of bicyclo[3.3.1]nonene (XII-XIV), and of bicyclo[3.2.1]octane (XV-XIX). Because of their simple hf patterns the esr spectra were easily interpreted. They come from either one of the two iminoxy radical isomers or overlapping of the two spectra of both isomers with different a^N values and almost equal *g* factors (a typical spectrum is given in Figure 1). Besides the iminoxy radicals, nitroxides[2d] whose structure is widely discussed elsewhere[5] appear too. The measured hfs constants and *g* factors of the studied iminoxy radicals are listed in Table I.

Stereochemistry of the Bicyclo[3.3.1]nonane System. The bicyclo[3.3.1]nonane system offers very interesting possibilities for stereochemical studies, because of its conformational peculiarities. Of the three possible conformers of bicyclo[3.3.1]nonane, representing relative energy minima, the most stable is the chair–chair one. This is true both for the parent hydrocarbon[6]
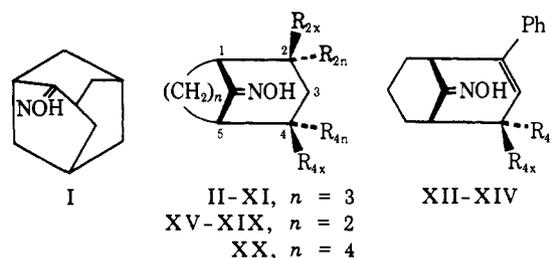
II, R$_{2n}$ = R$_{4n}$ = R$_{2x}$ = R$_{4x}$ = H
III, R$_{2x}$ = R$_{4n}$ = R$_{4x}$ = H; R$_{2n}$ = *N*-morpholinyl
IV, R$_{2x}$ = R$_{4x}$ = H; R$_{2n}$ = R$_{4n}$ = Ph
V, R$_{2x}$ = R$_{4x}$ = H; R$_{2n}$ = *N*-morpholinyl; R$_{4n}$ = Ph
VI, R$_{2n}$ = R$_{4n}$ = R$_{4x}$ = H; R$_{2x}$ = *N*-morpholinyl
VII, R$_{2n}$ = R$_{4n}$ = H; R$_{2x}$ = *N*-morpholinyl; R$_{4x}$ = Ph
VIII, R$_{2n}$ = R$_{4n}$ = H; R$_{2x}$ = *N*-morpholinyl; R$_{4x}$ = Me
IX, R$_{2x}$ = R$_{4n}$ = H; R$_{2n}$ = Ph; R$_{4x}$ = Ph
X, R$_{2x}$ = R$_{4n}$ = H; R$_{2n}$ = *N*-morpholinyl; R$_{4x}$ = Ph
XI, R$_{2n}$ = R$_{4x}$ = H; R$_{2x}$ = *N*-morpholinyl; R$_{4n}$ = Me
XII, R$_{4n}$ = R$_{4x}$ = H
XIII, R$_{4n}$ = H; R$_{4x}$ = Ph
XIV, R$_{4x}$ = H; R$_{4n}$ = Ph
XV, R$_{2n}$ = R$_{4n}$ = R$_{2x}$ = R$_{4x}$ = H
XVI, R$_{2x}$ = R$_{4n}$ = R$_{4x}$ = H; R$_{2n}$ = *N*-morpholinyl
XVII, R$_{2n}$ = R$_{4x}$ = H; R$_{2n}$ = *N*-morpholinyl; R$_{4n}$ = Ph
XVIII, R$_{2n}$ = R$_{4n}$ = R$_{4x}$ = H; R$_{2x}$ = *N*-morpholinyl
XIX, R$_{2x}$ = R$_{4n}$ = H; R$_{2n}$ = *N*-morpholinyl; R$_{4x}$ = Ph
XX, R$_{2n}$ or R$_{2x}$ = *N*-morpholinyl; R$_{4n}$ or R$_{4x}$ = Ph

and for bicyclo[3.3.1]nonan-9-one.[6d,7] However, due to some interactions (nonbonded repulsions, torsional, and angle strains[8]), the energy content of the chair-chair conformation is only with 2.7 kcal/mol[8,9] less than that of the chair-boat one. The energy difference between the two conformations must be even smaller for the corresponding 9-keto compound, as the flagpole interaction in its chair-boat conformation is missing. Therefore, an adequate substitution in one of the rings might shift the conformational equilibrium toward the

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(2) (a) A. Caragheorgheopol, M. Hartmann, R. Kühmstedt, and V. E. Sahini, *Tetrahedron Lett.*, 4161 (1967); (b) A. Caragheorgheopol, U. Gräfe, M. Hartmann, V. E. Sahini, and K. Wermann, *ibid.*, 3035 (1970); (c) H. Căldăraru, N. Barbulescu, L. Ivan, and V. E. Sahini, *ibid.*, 3039 (1970); (d) H. Căldăraru and M. Moraru, *ibid.*, 3183 (1971).
(3) (a) M. F. Chiu, B. C. Gilbert, and B. T. Sutcliffe, *J. Phys. Chem.*, 76, 553 (1972), and references therein; (b) H. Căldăraru, A. Caragheorgheopol, and V. E. Sahini, *J. Magn. Resonance*, 11, 335 (1973).
(4) H. M. McConnell, *J. Chem. Phys.*, 28, 1188 (1958).
(5) A. Caragheorgheopol, H. Căldăraru, T. Constantinescu, and V. E. Sahini, *J. Amer. Chem. Soc.*, 93, 6766 (1971).

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(7) (a) N. C. Webb and M. R. Becker, *J. Chem. Soc. B*, 1317 (1967); (b) L. Seamans, A. Moscowitz, G. Barth, E. Bunnenberg, and C. Djerassi, *J. Amer. Chem. Soc.*, 94, 6464 (1972).
(8) (a) G. J. Gleicher and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, 89, 582 (1967); (b) N. L. Allinger, J. A. Hirsch, M. A. Miller, I. J. Tyminski, and F. A. Van-Catledge, *ibid.*, 90, 1199 (1968); (c) N. L. Allinger, M. T. Tribble, M. A. Miller, and D. H. Wertz, *ibid.*, 93, 1637 (1971).
(9) (a) R. A. Appleton, C. Egan, J. M. Evans, S. H. Graham, and J. R. Dixon, *J. Chem. Soc. C*, 1110 (1968); (b) E. N. Marvell and R. S. Knutson, *J. Org. Chem.*, 35, 388 (1970).
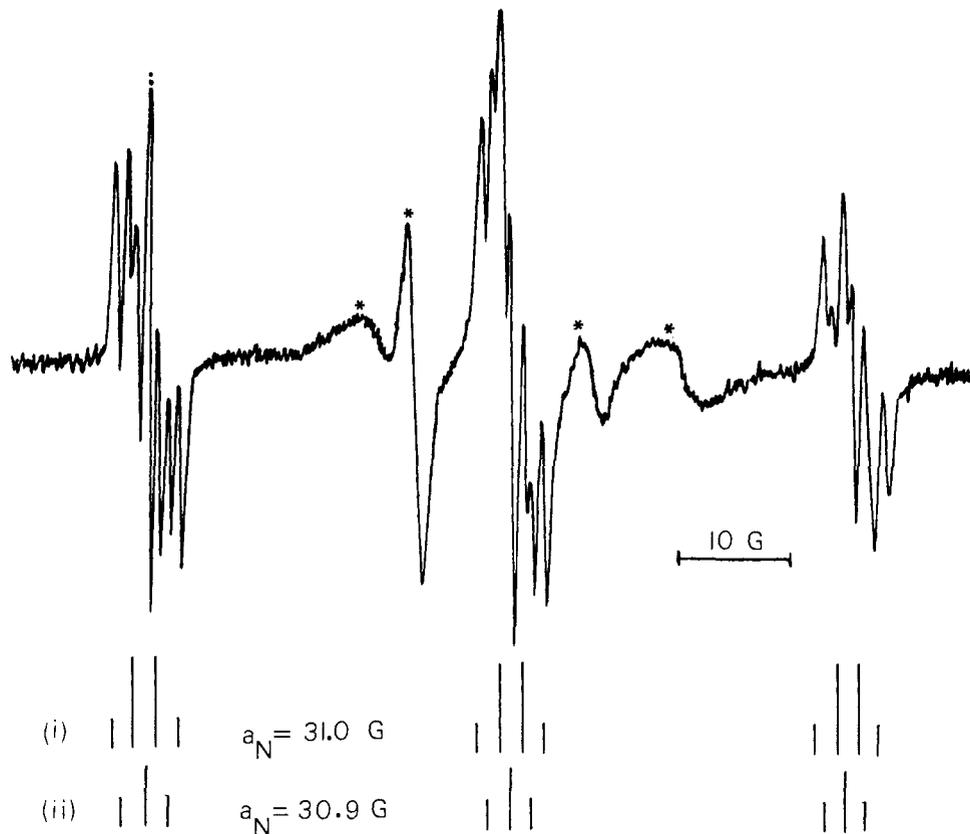
Figure 1. X-band spectrum of the iminoxy radical isomers i and ii obtained from IX. The marked lines belong to nitroxide radicals.

chair–boat conformation. Most of the conformational studies undertaken in this field have been focused on the effect of the substitution at endo C-3 as a possible factor of such a shifting.[9,10] We considered it interesting to extend these investigations to the 2 and 2,4 substitution effect, more so as no information existed about this effect in bicyclic systems. The works which could have dealt with this problem[11] have not treated the conformational aspects.

For the symmetrical compound II a single iminoxy radical was found (a^N = 30.2 G);[2b] it shows interaction with three equivalent protons (a^H = 1.9 G). According to what Gilbert and Norman found for the β-equatorial hydrogen hfs constant (a^H = 2.0 G) in non-flipping cyclohexane systems (XXI and XXII),[12] the iminoxy radical obtained from II was assigned chair–chair conformation XXIII. Since the same hydrogen hfs values might hypothetically appear for a chair–boat or even boat–boat conformation we obtained the im-

inoxy radical XXIV from adamantanone oxime, a compound which is forced to adopt the chair–chair conformation. As the number of interacting protons and their hfs constants are identical with those of radical XXIII, we confirm now the assigned chair–chair conformation of XXIII (the above results established by esr are in good agreement with those obtained by Parker et al.,[6d] for the bicyclo[3.3.1]nonan-9-one from ir data).
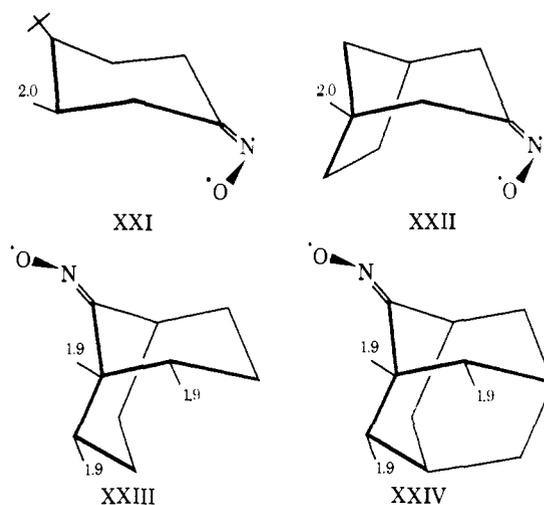
These two iminoxy radicals (XXIII and XXIV) have been chosen as model compounds for all configuration and conformation assignments of the other substituted iminoxy radicals. The assignments are based on the following remarkable facts: (i) the interacting protons are those syn to the iminoxy group oxygen; (ii) all hydrogen hfs constants of studied iminoxy radicals have the same value no matter the nature of the substituents

(10) (a) M. Fisch, S. Smallcombe, J. C. Gramain, M. A. McKervey, and J. E. Anderson, J. Org. Chem., 35, 1886 (1970); (b) W. D. K. Macrosson, J. Martin, and W. Parker, Tetrahedron Lett., 2589 (1965); (c) J. A. Peters, J. D. Remijnse, A. v. Wiele, and H. v. Bekkum, ibid., 3065 (1971); (d) I. Fleming, S. W. Hanson, and J. K. M. Sanders, ibid., 3733 (1971); (e) E. N. Marvell, G. J. Gleicher, D. Sturmer, and K. Salisbury, J. Org. Chem., 33, 3393 (1968); (f) W. N. Speckamp, J. Dijkink, A. W. K. D. Dekkers, and H. O. Huisman, Tetrahedron, 27, 3143 (1971); (g) C. Y. Chen and R. J. W. Le Fèvre, J. Chem. Soc. B, 539 (1966); (h) M. R. Vegar and R. J. Wells, Tetrahedron Lett., 2847 (1971); (i) H. S. Aaron, C. P. Ferguson, and C. P. Rader, J. Amer. Chem. Soc., 89, 1431 (1967); (j) J. McEuen, R. P. Nelson, and R. G. Lawton, J. Org. Chem., 35, 690 (1970).

(11) (a) C. S. Dean, J. R. Dixon, S. H. Graham, and D. O. Lewis, J. Chem. Soc. C, 1491 (1968); (b) R. A. Appleton, K. H. Baggaley, C. Egan, J. M. Davies, S. H. Graham, and D. O. Lewis, ibid., 2032 (1968); (c) V. Dressler and K. Bodendorf, Justus Liebigs Ann. Chem.. 720, 71 (1968); (d) H. M. Hellman, R. A. Jerussi, and J. Lancaster, J. Org. Chem., 32, 2148 (1967).

(12) B. C. Gilbert and R. O. C. Norman, J. Chem. Soc. B, 86 (1966).

Table I. Parameters of the Esr Spectra of the Iminoxy Radicals

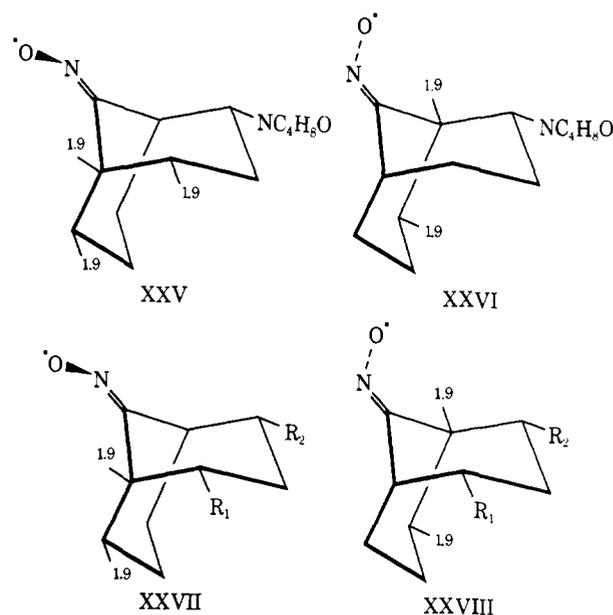| Parent oximes	a^N	a^H	No. of protons	g
I	30.6	1.9	3	2.0065
II	30.2	1.9	3	2.0064
III				
(i)	30.6	1.9	3	2.0063
(ii)	31.4	1.9	2	2.0063
IV	30.8	1.9	2	2.0063
V	30.8	1.9	2	2.0065
VI				
(i)	31.1	1.9	2	2.0062
(ii)	31.3	1.9	2	2.0065
VII[a]	30.7	1.9	2	2.0065
VIII	30.7	1.9	2	2.0065
IX				
(i)	31.0	1.9	3	2.0064
(ii)	30.9	1.9	2	2.0063
X[a]				
(i)	30.8	1.9	3	2.0064
(ii)	31.6	1.9	2	2.0064
XI[a]				
(i)	30.6	1.9	3	2.0063
(ii)	31.5	1.9	2	2.0063
XII				
(i)	30.1	1.9	3	2.0064
(ii)	30.7	1.9	2	2.0063
XIII				
(i)	30.0	1.9	3	2.0064
(ii)	30.8	1.9	2	2.0063
XIV	30.4	1.9	2	2.0064
XV	30.4	1.9	3	2.0065
XVI	30.1	1.9	3	2.0065
XVII	30.1	1.9	2	2.0064
XVIII	30.0	1.9	3	2.0065
XIX[a]				
(i)	30.2	1.9	3	2.0065
(ii)	31.1	1.9	2	2.0065
XX	30.8	2.0	1	
		1.6	1	
		0.5	2	

[a] The configuration at the 2 position established in this work.

(see Table I); (iii) the number of interacting protons gives the desired information.

Of the two iminoxy radicals obtained from III, that which shows interaction with three protons (a^N = 30.6 G, a^H = 1.9 G (3)) is assigned structure XXV; the other one which shows interaction with two protons (a^N = 31.4 G, a^H = 1.9 G (2)) is its geometrical isomer XXVI. The iminoxy radical obtained from IV shows interaction with two protons (a^N = 30.8 G, a^H = 1.9 G (2)) and is assigned structure XXVII (R_1 = R_2 = Ph), while for the iminoxy radical of V can be assigned either structure XXVII (R_1 = Ph, R_2 = NC_4H_8O) or structure XXVIII (R_1 = Ph, R_2 = NC_4H_8O). All these radicals (with endo-2 or endo,endo-2,4 substitution) have a chair–chair conformation as compared to the model radicals XXIII and XXIV, the missing of one interacting proton in radicals XXVI, XXVII, and XXVIII being due to the corresponding equatorial proton substitution.

The similar results obtained for the iminoxy radicals from some substituted tricyclo[7.3.1.0^{2,7}]tridecan-13-one oximes extend these conclusions over the conformation of those radicals.[2c]

From the exo-2-(N-morpholinyl)bicyclo compound VI both iminoxy radical isomers ((i) a^N = 31.1 G, a^H = 1.9 G (2); (ii) a^N = 31.3 G, a^H = 1.9 G (2)) are obtained. If they had the chair–chair conformation they would have shown three interacting protons as the rad-

icals XXIII and XXIV do. The presence of only two interacting protons in both isomers is evidence of a preferential chair–boat conformation for this framework. For a bulky substituent (as morpholinyl is) in the exo-2 position, the 2,4-diaxial interaction present in the chair–chair conformation imposes on the bicyclo[3.3.1]-nonane system (sp^2 hybridization at C-9) to adopt a chair–boat conformation. Therefore, the iminoxy radical isomers i and ii from VI can be assigned structures XXIX (R_1 = H, R_2 = NC_4H_8O) and XXX (R_1 = H, R_2 = NC_4H_8O) (or XXX and XXIX), respectively.[13]
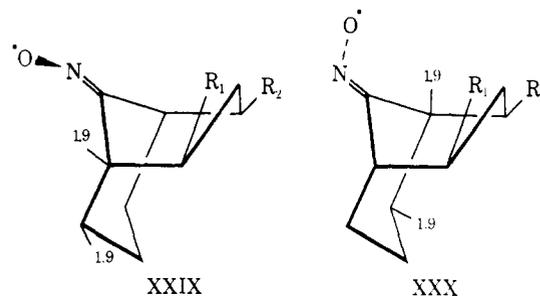
To prove if a chair-boat–chair-chair conformational equilibrium[14] can be stimulated by temperature, a study of variation with temperature was carried out for the radicals obtained from VI. In the range room temperature–40° (above this temperature the radicals rapidly disappear) the pattern of the spectrum remains unchanged, indicating that the room temperature conformational equilibrium (shifted toward chair–boat form) is not altered by temperature.

Interesting conclusions about the behavior of different substituents in the exo-2 position arise from the works of Ganter, et al.,[15] and Kraus, et al.[16] Their ir
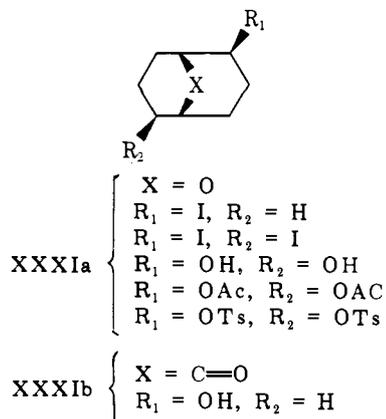
(13) The above mentioned result can be extended to exo,exo-2-(N-morpholinyl)-7-tert-butylbicyclo[3.3.1]nonan-9-one.[11b]

(14) If such an equilibrium occurred the pattern of the spectrum should drastically change because the equilibrium involves two species with different number of interacting protons.

(15) (a) C. Ganter, K. Wicker, W. Zwahlen, and K. S. Sabba, Helv. Chim. Acta, 53, 1618 (1970); (b) C. Ganter, R. O. Duthaler, and W. Zwahlen, ibid., 54, 578 (1971); (c) R. O. Duthaler, K. Wicker, P. Ackermann, and C. Ganter, ibid., 55, 1809 (1972).

(16) W. Kraus, W. Rothenwöhrer, and R. Chassin. Tetrahedron Lett., 4581 (1969).

XXV

XXVI

XXVII

XXVIII

XXIX

XXX

and nmr data for *exo*-2- and *exo,exo*-2,6-substituted-9-oxabicyclo[3.3.1]nonanes (XXXIa) and for the *exo*-2-hydroxybicyclo[3.3.1]nonan-9-one (XXXIb) seem to indicate that these compounds prefer a chair–chair conformation. Webb and Becker[7a] found by X-ray the same conformation for the *exo*-2-chlorobicyclo[3.3.1]-nonan-9-one (in this case one can assume that the same conformation preserves in solution[6c]). It follows that there is a critical dimension of the exo-2 substituent which shifts the conformational equilibrium toward the chair–boat form. The different behavior of these substituents (R_1 = Cl, I, OH, OAc, OTs) relative to the morpholinyl[17] is somehow expected, as their conformational energy in cyclohexane is small (0.4–0.8 kcal/mol[18]).

$$R_1$$

$$X$$

$$R_2$$

$$\text{XXXIa} \begin{cases} X = O \\ R_1 = I, \ R_2 = H \\ R_1 = I, \ R_2 = I \\ R_1 = OH, \ R_2 = OH \\ R_1 = OAc, \ R_2 = OAC \\ R_1 = OTs, \ R_2 = OTs \end{cases}$$

$$\text{XXXIb} \begin{cases} X = C{=}O \\ R_1 = OH, \ R_2 = H \end{cases}$$

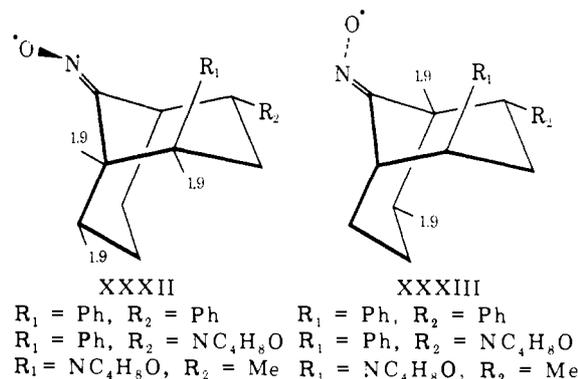From each of the exo,exo-2,4 disubstituted compounds VII and VIII a single iminoxy radical isomer was obtained. They both show interaction with two protons (a^N = 30.7 G, a^H = 1.9 G (2)); the absence of the third interacting proton from their pattern as compared to the radicals XXIII and XXIV indicates that they undoubtedly adopt the chair–boat conformation and are assigned either structure XXIX (R_1 = Ph or Me, R_2 = NC_4H_8O) or XXX (R_1 = Ph or Me, R_2 = NC_4H_8O). All endo,exo disubstituted compounds IX, X, and XI gave both iminoxy radical isomers i and ii; one of them (the isomer i) showing interaction with three protons is assigned structure XXXII, the other one (the isomer ii) interacting only with two protons has structure XXXIII. All these radicals, indifferent of the pair (endo,exo) of substituents, have a chair–chair conformation as the number of interacting protons indicates.

For the radicals obtained from IX we tried to excite with temperature a chair-chair–chair-boat equilibrium.[14] The pattern of the spectrum remains unchanged in the range room temperature–120°, indicating that the preferred chair–chair conformation of the radicals is not affected by temperature.

The configuration at the 2 and 2,4 positions is well established in the literature for most of the studied parent ketones (oximes respectively). However, some difficulties arise in the configurational assignments at the 2 position for some of the compounds (V, VII, VIII, X, and XI). In this work we were able to establish the configuration at this position for VII, X, and

(17) For lack of conformational energy data of the morpholinyl, one can use in a good approximation the value of 2.1 kcal/mol[18] of the cyclohexyl.

(18) J. A. Hirsch, *Top. Stereochem.*, **1**, 199 (1967).

XXXII

R_1 = Ph, R_2 = Ph
R_1 = Ph, R_2 = NC_4H_8O
R_1 = NC_4H_8O, R_2 = Me

XXXIII

R_1 = Ph, R_2 = Ph
R_1 = Ph, R_2 = NC_4H_8O
R_1 = NC_4H_8O, R_2 = Me

XI independent of nmr and chemical results.[19] Our assignments arrive at the same conclusions as those obtained by the two methods. All the assignments are based on the properties of the studied iminoxy radicals already mentioned above and on the fact that the configuration at the 4 position is firmly established[19] by other methods. Thus, of the three isomers of the 2-(*N*-morpholinyl)-4-phenylbicyclo[3.3.1]nonan-9-one oxime obtained by synthesis, two isomers (namely VII and X) have the phenyl substituent in the exo-4 position (as established from nmr[19] and chemical[11c] evidences) and differ by the configuration at the 2 position. Since one of them (X) gave both iminoxy radical isomers i (a^N = 30.8 G, a^H = 1.9 G (3)) and ii (a^N = 31.6 G, a^H = 1.9 G (2)) the configuration at the 2 position was easy to be assigned: the isomer i showing interaction with three protons has the iminoxy group oxygen syn to the *exo*-4-phenyl substituent; the other one (ii) presenting only two interacting protons must have the iminoxy group oxygen syn to the morpholinyl substituent in the endo-2 position. So, the parent compound which produced these two iminoxy radical isomers has the configuration X. Its pair differing only by configuration at the 2 position has structure VII. Our configurational assignments established by esr as well as by nmr and chemical methods[19] are contradictory to those found by Dressler and Bodendorf[11c] and Graham, *et al.*[11b] They found that the major product of reaction between cinnamaldehyde and 1-(*N*-morpholinyl)cyclohexene is *endo*-2-(*N*-morpholinyl)-*exo*-4-phenylbicyclo[3.3.1]nonan-9-one. Our results indicate for the major product of this reaction (VII) the same configuration at the 4 position as these authors found, but the configuration at the 2 position inverted (the disagreement between these results is largely explained elsewhere[19]).

The configuration at the 2 position in compound XI has been established the same way.

Stereochemistry of the Bicyclo[3.3.1]nonene System. If in the cyclohexen-4-one there are still some degrees of freedom of the ring mobility, they disapper by including the ketone group in the bridge of bicyclo[3.3.1]non-2-ene (the cyclohexene ring becoming completely rigid). Thus, this system will adopt, no matter what the substitution (pseudoequatorial or pseudoaxial) in the cyclohexene ring, a chair–half-chair conformation. Our esr results confirm this as indicated by the number of interacting protons in the assigned structures[2d] XXXIV (R = Ph or H) and XXXV (R = Ph or H) for the iminoxy radical isomers i and ii, respectively,

(19) N. Barbulescu and M. Moraru, *Rev. Roum. Chim.*, in press.

obtained from XII and XIII, as well as in the structure XXXVI or XXXVII for the radical obtained from XIV.

XXXIV   XXXV

XXXVI   XXXVII
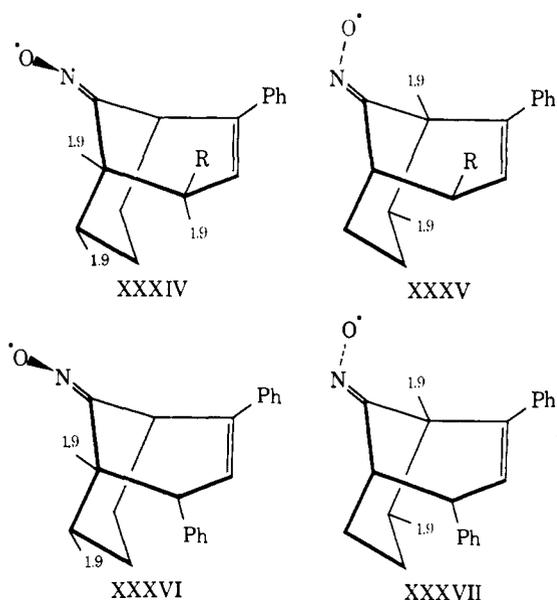
Stereochemistry of the Bicyclo[3.2.1]octane System.

This system is less interesting than the bicyclo[3.3.1]-nonane one, because of the absence of the steric compressions due to the 3,7 interactions. However, some new information might be worthwhile for completing the picture of the behavior of this framework. Most interesting should be to compare the effect of the substituent in the exo-2 position on the conformation of this system relative to the same effect in the bicyclo-[3.3.1]nonane one. As it will result below, the introduction of the morpholinyl substituent in the exo-2 position of the bicyclo[3.2.1]octane system (sp^2 hybridization at C-8) leaves the six-membered ring in the chair form, unlike the findings for the bicyclononane system, indicating the strains in the latter responsible for shifting the energy balance toward the boat form (the reflex effect[20] was neglected in this discussion).
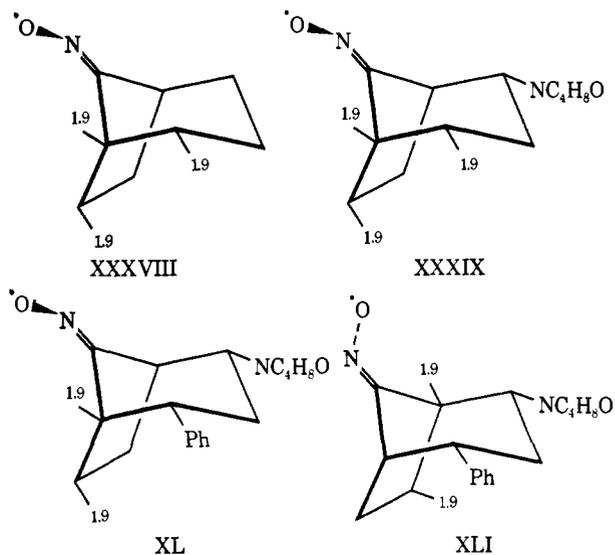
As for the bicyclo[3.3.1]nonane system, we used in our assignments a symmetrical model compound, XV. The iminoxy radical obtained from this compound shows interaction with three protons (a^N = 30.4 G, a^H = 1.9 G (3))[21] and is assigned structure XXXVIII.

The single iminoxy radical obtained from XVI, showing interaction with three protons (a^N = 30.1 G, a^H = 1.9 G (3)), is assigned structure XXXIX, while for the radical obtained from XVII (interaction with two protons (a^N = 30.1 G, a^H = 1.9 G (2))) is assigned either structure XL or XLI. All these radicals have the six-membered ring in the chair conformation, as compared to the model radical XXXVIII.

When introducing the morpholinyl substituent in the exo-2 position (compound XVIII), the iminoxy radical obtained (a^N = 30.0 G, a^H = 1.9 G (3)) showing interaction with three protons has to be assigned either structure XLII or XLIII; in this case the six-membered ring preserves the chair conformation, the boat conformation being excluded since the radical with such a

XXXVIII   XXXIX

XL   XLI

conformation should have shown only two interacting protons (see structures XXIX and XXX).

The compound XIX gave both iminoxy radical isomers; one of them (i) showing interaction with three protons (a^N = 30.2 G, a^H = 1.9 G (3)) has structure XLIV, the other one (ii) (interaction only with two protons) (a^N = 31.1 G, a^H = 1.9 G (2)) is its geometrical isomer XLV.

XLII   XLIII

XLIV   XLV
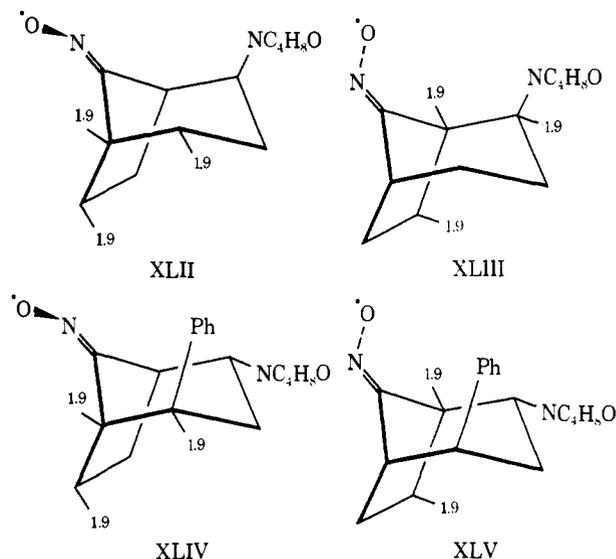
The configuration at the 2 position for XIX could be assigned (knowing the configuration at the 4 position[22]) in the same way as for X (see above).

All the results obtained on the conformation of the studied iminoxy radicals can be extended with the greatest confidence to the corresponding ketones, as the small differences between the iminoxy group and carbonyl group are insignificant from the stereochemical point of view.

The relatively great number of studied iminoxy radicals allows us to extract some conclusions which might be worthwhile for clearing up the spin density transmission in σ radicals.

(i) The α-equatorial proton always has 1.9 G hfs; this is consistent with 1.7 G hfs found by Russell and

(20) J. Fournier and B. Waegell, *Tetrahedron*, **28**, 3407 (1972), and references therein.

(21) The same radical previously obtained in our laboratory was considered to have hyperfine interaction only with two equivalent protons[2b] based on poorly resolved spectra.

(22) N. Bărbulescu and M. Moraru, *Rev. Chim. (Bucharest)*, **23**, 457 (1972).

Mackor[23] for the same proton in a series of rigid cyclohexanone iminoxy radicals.

(ii) The hfs constant of the β-equatorial (or pseudoequatorial) proton has always the same value (1.9 G). This result together with the absence of a measurable hfs value for the β-axial proton in the chair conformation and for any of the β protons in the boat conformation indicate a certain geometry of the $\cdot$ONCCCH fragment for a favorable σ spin density transmission (although the double bond in the bicyclo[3.3.1]nonene system and the five-membered ring in the bicyclo[3.2.1]octane may introduce some distortions of the framework as compared to the bicyclo[3.3.1]nonane system, the geometry of this fragment seems to be only slightly modified).

Experimental Section

Preparation of the Radicals. The radicals were generated in the sample tube by adding benzene to the oxime–lead tetraacetate mixture. The very unstable radicals (those obtained from the bicyclo[3.2.1]octan-8-one oximes) were prepared using partly decomposed lead tetraacetate and the oxime deposited (by evaporating from a benzene solution) on porous Vycor glass.

Esr Spectra. All esr spectra were recorded on a JES-3B (JEOL) spectrometer with 100-kHz field modulation using X-band frequency. Some of the spectra were also recorded in K-band frequency. The hfs constants and g factors were measured by comparison with potassium peroxylamine disulfonate ($a^N = 13.0$ G, $g = 2.0055$).

Methods and Materials. Infrared spectra were measured on a UR-20 C. Zeiss-Jena spectrometer. Nuclear magnetic resonance spectra were obtained with a Varian A-60A spectrometer using tetramethylsilane as an internal standard.

Lead tetraacetate was prepared as described in the literature.[24] Benzene was dried on sodium wires and distilled. The oximes were prepared from the corresponding bicyclic ketones by usual methods. All of them gave satisfactory C, N, and H analysis.

2-Adamantanone (I)[25] was purchased from Aldrich Chemical Co. 2-Phenylbicyclo[3.3.1]non-2-en-9-one (XII), 2,4-diphenylbicylo[3.3.1]non-2-en-9-ones (XIII and XIV), and 2,4-diphenylbicyclo[3.3.1]-nonan-9-ones (IV and IX) were prepared as described in the literature.[26] Only the last two isomers (mp 143 and 146°, respectively) of the 2,4-diphenylbicyclo[3.3.1]nonan-9-one were obtained in the hydrogenation product (2% Pd/sodium silicate as catalyst) of the corresponding bicyclo[3.3.1]non-2-en-9-ones.

All morpholinyl substituted bicyclic ketones were synthesized by Stork cyclization.[27]

The reaction of acraldehyde with 1-(N-morpholinyl)cyclopen-

tene[28] afforded a 2:3 mixture of XVI and XVIII which were separated on alumina (Brockmann) with petroleum ether–ethylic ether.

endo-2-(N-Morpholinyl)bicyclo[3.2.1]octan-8-one (XVI): n^{25}D 1.5157; methiodide mp 198–201°; ir (CHCl₃) 1451, 1468, 1478, and 1749 cm⁻¹; nmr δ (CCl₄) 2.44 (t, 4), 2.62 (q, 1), and 3. 58 (t, 4).

exo-2-(N-Morpholinyl)bicyclo[3.2.1]octan-8-one (XVIII): n^{25}D 1.5152; methiodide mp 230–232°; ir (CHCl₃) 1465, 1482, and 1746 cm⁻¹; nmr δ (CCl₄) 2.44 (t, 4) and 3.58 (t, 4).

In the reaction of acraldehyde with 1-(N-morpholinyl)cyclohexene the 2-(N-morpholinyl)bicyclo[3.3.1]nonan-9-ones (III and VI) were obtained as described.[11a]

endo-2-(N-Morpholinyl)bicyclo[3.3.1]nonan-9-one (III): n^{25}D 1.5163 (lit.[11a] n^{25}D 1.5165); methiodide mp 218–220° (lit.[11a] mp 196–198°); ir (CHCl₃) 1445, 1459, 1492, 1725, and 2992 cm⁻¹; nmr δ (CCl₄) 2.42 (t, 4) and 3.61 (t, 4).

exo-2-(N-Morpholinyl)bicyclo[3.3.1]nonan-9-one (VI): n^{25}D 1.5160 (lit.[11a] n^{25}D 1.5165); methiodide mp 225–226° (lit.[11a] mp 215–216°); ir (CHCl₃) 1457 and 1724 cm⁻¹; nmr δ (CCl₄) 2.43 (t, 4), 2.82 (o, 1), and 3.57 (t, 4).

From the reaction product of crotonaldehyde with 1-(N-morpholinyl)cyclohexene[19] two isomers of 2-(N-morpholinyl)-4-methylbicyclo[3.3.1]nonan-9-one (VIII and XI) were separated on alumina (Brockmann) with petroleum ether–ethylic ether. The fast running component (XI) represented 15–20% of the mixture. The two amino ketone isomers differed by the C-4 configuration resulting in two 4-methylbicyclo[3.3.1]nonan-2-ones.[19]

exo,exo-2,4-(N-Morpholinyl)methylbicyclo[3.3.1]nonan-9-one (VIII): ir (CHCl₃) 1457, 1472, 1707, and 1713 cm⁻¹; nmr δ (CCl₄) 1.04 (d, 3), 2.44 (m, 4), 2.86 (o, 1), and 3.57 (m, 4).

exo-2-(N-Morpholinyl)-*endo*-4-methylbicyclo[3.3.1]nonan-9-one (XI): ir (CHCl₃) 1446, 1458, 1491, 1710, and 2994 cm⁻¹; nmr δ (CCl₄) 1.06 (d, 3), 2.42 (t, 4), and 3.61 (t, 4).

The reaction of cinnamaldehyde with 1-(N-morpholinyl)cyclopentene[22] yielded two isomers of 2-(N-morpholinyl)-4-phenylbicyclo[3.2.1]octan-8-one (XVII and XIX).

endo,endo-2,4-(N-Morpholinyl)phenylbicyclo[3.2.1]octan-8-one (XVII): mp 129–130°; methiodide mp 235–237°; ir (KBr) 1455, 1473, 1480, and 1746 cm⁻¹; nmr δ (CCl₄) 2.50 (t, 4), 3.10 (o, 1), and 3.60 (t, 4).

endo-2-(N-Morpholinyl)-*exo*-4-phenylbicyclo[3.2.1]octan-8-one (XIX): mp 113–113.5°; methiodide mp 219–220°; ir (KBr) 1459, 1480, and 1749 cm⁻¹; nmr δ (CCl₄) 2.44 (t, 4), 2.78 (o, 1), 3.23 (m, 1), and 3.58 (t, 4).

endo,endo-2,4-(N-Morpholinyl)phenyl-, *exo,exo*-2,4-(N-morpholinyl)phenyl-, and *endo*-2-(N-morpholinyl)-*exo*-4-phenylbicyclo[3.3.1]nonan-9-one (V, mp 145°; VII, mp 130°; and X, mp 95°, respectively) were obtained in reaction of cinnamaldehyde with 1-(N-morpholinyl)cyclohexene as described in the literature.[11c] The major product of this reaction was *exo,exo*-2,4-(N-morpholinyl)-phenylbicyclo[3.3.1]nonan-9-one (VII, mp 130°).

2-(N-Morpholinyl)-4-phenylbicyclo[4.3.1]decan-10-one (XX) was obtained as the major product in the reaction of cinnamaldehyde with 1-(N-morpholinyl)cycloheptene:[19] mp 112–113°; methiodide mp 192–194°; ir (KBr) 1418, 1461, and 1724 cm⁻¹; nmr δ (CCl₄) 2.48 (t, 4), 2.7–3.1 (m, 2), and 3.57 (t, 4).

(23) G. A. Russell and A. Mackor, *J. Amer. Chem. Soc.*, **96**, 145 (1974).

(24) "Handbook of Preparative Inorganic Chemistry," G. Brauer, Ed., Academic Press, New York, N. Y., 1963, p 488.

(25) All the numbers in parentheses refer to the corresponding oximes.

(26) A. C. Cope and E. C. Herman, *J. Amer. Chem. Soc.*, **72**, 3405 (1950).

(27) G. Stork and H. K. Landesman, *J. Amer. Chem. Soc.*, **78**, 5129 (1956).

(28) (a) N. A. Le Bel and L. A. Spurlock, *Tetrahedron*, **20**, 215 (1964); (b) C. S. Foote and R. B. Woodward, *ibid.*, **20**, 687 (1964).