Conformational Studies by Dynamic Nuclear Magnetic Resonance. Part X.[1] Stereodynamics and Conformations of Hindered Triazenes

By **Lodovico Lunazzi,*** Istituto di Chimica Organica, Universitá, Risorgimento 4, Bologna, Italy
Giovanni Cerioni, Istituto di Chimica Farmaceutica, Universitá, Cagliari, Italy
Elisabetta Foresti, Istituto di Mineralogia e Petrografia, Universitá, Bologna, Italy
Dante Macciantelli, Laboratorio C.N.R., Ozzano Emilia, Bologna, Italy

Rotational barriers about the N(1)–N(2) bond in a number of 1,1-dialkyl-3-aryltriazenes ($R_2N{\cdot}N{:}NAr$) have been measured by line-shape analysis of the n.m.r. signals. It has been observed that the barrier is only slightly affected by the bulkiness of the alkyl groups but is substantially lowered when the triazenes contain the piperidyl ring with two (DMP) or four (TMP) methyl groups in positions 2 and 6. This feature is explained in the DMP derivatives as being due to the repulsion of the two axial *cis*-methyl groups; this conformation has been confirmed by *X*-ray diffraction. In TMP derivatives, the lowering of the barrier can be explained by assuming a non-chair (twisted) conformation for the piperidyl ring in solution. ^{13}C N.m.r. spectra also seem to support this conformation.

IN previous parts of this series [2,3] it has been reported that hydrazones containing the 2,2,6,6-tetramethylpiperidyl (TMP) ring experience restricted rotation about the N–N bond.[2,3] When the less-hindered 2,6-*cis*-dimethylpiperidyl (DMP) ring is present the phenomenon cannot be observed.[2] It has been shown that in the first case the molecule is forced into a ' perpendicular '

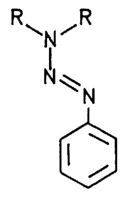
[1] Part 9, L. Lunazzi, A. Dondoni, G. Barbaro, and D. Macciantelli, *Tetrahedron Letters*, 1977, 1079.

[2] L. Lunazzi, G. Cerioni, and K. U. Ingold, *J. Amer. Chem. Soc.*, 1976, **98**, 7484.

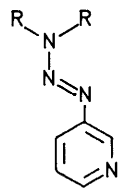
[3] L. Lunazzi, G. Placucci, and G. Cerioni, *J.C.S. Perkin II*, 1977, 1666.

conformation, which causes a quite hindered rotational motion. In the DMP hydrazones the conformation is most likely planar [2] and the weakness of the partial N–N double-bond character in the N·N:C moiety makes the NN-rotation almost unhindered.

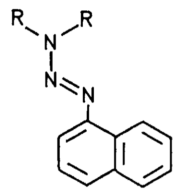
However, 1,1-dialkyl-3-aryltriazenes $R_2N{\cdot}N{:}NAr$ are known [4-6] to have a greater N(1)–N(2) double-bond character, and restricted rotation is more easily detectable. We have therefore investigated TMP and DMP aryl triazenes, together with less-hindered derivatives,



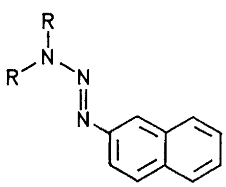
(1) R = Me
(2) R = Et
(3) R = Pr^i



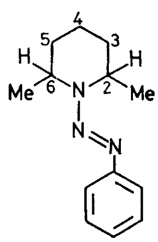
(4) R = Me
(5) R = Et
(6) R = Pr^i



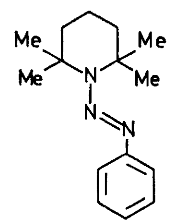
(7) R = Me
(8) R = Pr^i



(9) R = Me
(10) R = Pr^i



(11)



(12)

to determine their stereochemical properties and to assess their differences with the aforementioned [2,3] hydrazones.

RESULTS AND DISCUSSION

In the molecules investigated (1)—(12) only one of the two possible configurations (*cis*, *trans*) has been detected at the N:N bond.

X-Ray diffraction of *p,p'*-dibromodiazoaminobenzene [7] and our own determination on (11) (see later) showed that the *trans*-configuration is adopted; as a consequence this was assumed for the entire series. All the triazenes investigated exhibit at low temperature diastereotopic alkyl groups, owing to the restricted rotation around the N(1)–N(2) partial double bond. The n.m.r. spectra allow the determination of the thermodynamic activation parameters through a total line-shape (t.l.s.) analysis of the spectra as functions of temperature.

In the cases of (1), (4), (7), (9), and (12), only two lines are observed at low temperature for the diastereotopic methyl groups: they broaden and coalesce when the temperature is raised. The appearance of the spectra is more complicated for the ethyl groups of (2) and (5), and for the isopropyl group of (3), (6), (8), (10), and (11). The spectra were all interpreted by computer simulation [8] of the methyl signals. Figure 1 shows sample spectra for the Me protons in the isopropyl group of compound (3).

TABLE 1

Free energies of activation (kcal mol^{-1}) for rotational barriers of triazenes (1)—(12) in CS_2. For derivatives (2) and (3) $\Delta H^‡$/kcal mol^{-1} and $\Delta S^‡$/cal mol^{-1} K^{-1}, were also determined; errors in $\Delta G^‡$ are *ca.* ± 0.1 kcal mol^{-1}

Cpd.	$\Delta G^‡$	Cpd.	$\Delta G^‡$
(1)	13.8	(8)	14.7
(2)	13.8 [a]	(9)	14.2
(3)	14.4 [b]	(10)	14.7
(4)	15.2	(11)	10.8
(5)	14.9	(12)	10.6
(6)	15.5	(13) [c]	19.6
(7)	14.4	(15) [c]	19.6

[a] $\Delta H^‡$ 14.3 ± 0.5, $\Delta S^‡ = 1.7 \pm 1.7$. [b] $\Delta H^‡ = 15.6 \pm 0.8$, $\Delta S^‡ = 4.5 \pm 2.6$. [c] From ref. 2.

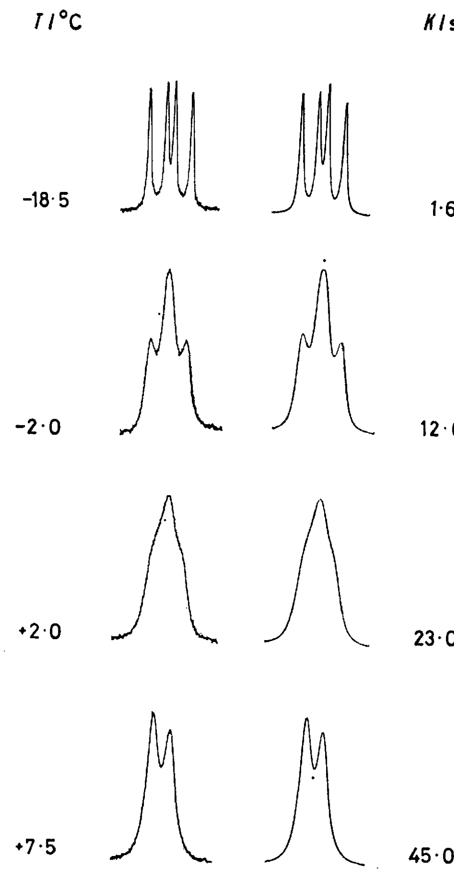
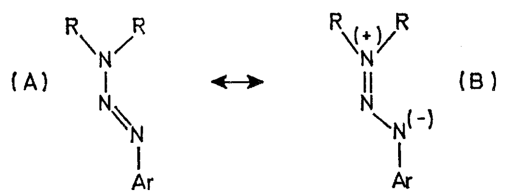


FIGURE 1 Experimental (left) and computer-simulated (right) 60 MHz n.m.r. spectra of the methyl signals of the isopropyl group of derivative (3) in CS_2 as a function of temperature. The difference in chemical shift between the methyl signals is 10.2 Hz and the J_{HH} values are 6.4_5 and 6.7_5 Hz (low- and high-field doublet, respectively)

[4] N. P. Marullo, C. B. Mayfield, and E. H. Wagener, *J. Amer. Chem. Soc.*, 1968, **90**, 510.
[5] M. H. A. Khtar, R. S. McDaniel, M. Feser, and A. C. Oechlschlager, *Tetrahedron*, 1968, **24**, 3899.
[6] G. Koga and J. P. Anselme, *Chem. Comm.*, 1969, 894.
[7] Y. D. Kondrashev, *Kristallografiya*, 1961, **6**, 515.
[8] G. Binsch and D. A. Kleier, Program DNMR, Q.C.P.E., Indiana University.

Thermodynamic parameters obtained from Eyring treatment of the rate constants in (2) and (3) are given in the footnote to Table 1. As observed in many other cases of restricted rotation [1-3,9-11] the $\Delta S^\ddagger$ values are almost negligible, within experimental error, so that the more easily measurable $\Delta G^\ddagger$ values can be used instead of $\Delta H^\ddagger$, as a measure of the rotational barrier.

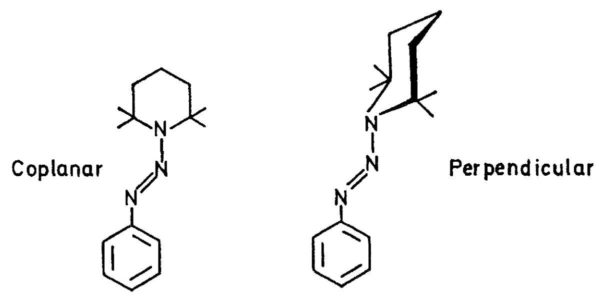
The large negative values for $\Delta S^\ddagger$ quoted in ref. 5 are likely to be due to errors involved in the determination of the rate constants, since various approximations [5] (instead of a t.l.s. analysis) were employed at different temperatures. We also detected a solvent effect on $\Delta G^\ddagger$, in that the values in $CDCl_3$ were found to be 1 kcal mol^{-1} smaller (see also ref. 4) than in CS_2. The latter being a nonpolar solvent, we considered it a more appropriate medium than $CDCl_3$, since it cannot develop specific interaction with the solute. The $\Delta G^\ddagger$ values obtained in CS_2 for (1)—(12) are reported in Table 1. As already observed [4,5] modifications in the electron-withdrawing properties of the aromatic ring affect the rotational barrier. Derivatives (4)—(6) have larger barriers than do (1)—(3), since the pyridyl ring * stabilizes structure (A) more than phenyl or naphthyl groups.



On the contrary, the effect of the bulkiness of the various substituents in (1)—(10) is quite small. In (1)—(3), as well as in (4)—(6), the $\Delta G^\ddagger$ values are only slightly affected when the size of R increases from Me to Et to Pr^i: the internal differences are not >0.5 kcal mol^{-1}. Also, the dimensions of the aromatic ring are not relevant, in that both the α- and β-naphthyl derivatives (7)—(10) have barriers very similar to those of the corresponding phenyltriazenes (1)—(3), a situation opposite to that observed in hydrazones with aromatic substituents.[3]

However, triazenes containing the 2,6-*cis*-dimethyl- or 2,2,6,6-tetramethyl-piperidyl ring [(11) and (12)] have much lower $\Delta G^\ddagger$ values; since we have shown that the size of the substituent does not influence the barrier to such a large extent, the reasons for this behaviour have to be sought in the conformational properties of the six-membered ring.

Before advancing any hypothesis on the effect of the ring conformation on the $\Delta G^\ddagger$ values, it has to be established whether the piperidyl ring is ' coplanar ' or ' perpendicular ' to the plane containing the N·N:N group.† Whereas for (11) [as for (1)—(10)] the observation of diastereotopic methyl (or alkyl) groups requires a ' coplanar ' conformation, in derivative (12) they can be diastereotopic even in a ' perpendicular ' conformation, as previously [2] demonstrated.



A clear-cut method for distinguishing between these two possibilities in solution is offered by ^{13}C n.m.r. spectra (Table 2) at a temperature at which N(1)–N(2) rotation is slow.[3] If the conformation is perpendicular only the methyl carbons of (12) should be diastereotopic [2,3] (*i.e.* mainly axial or mainly equatorial), whereas if the conformation is planar the 2,6- and 3,5-carbons should also be nonequivalent. Figure 2 shows the ^{13}C n.m.r. spectra of (11) and (12) at 25 and −80 °C. Whereas at 25 °C there are only 4 signals due to the aliphatic carbons, at −80 °C they are split into pairs [with the obvious exception of C(4)]. It can be thus concluded that (12), and also (11), is in a ' coplanar ' conformation, thus differing from the analogous hydrazones.[3]

TABLE 2

^{13}C Chemical shifts (from tetramethylsilane; p.p.m. at 25.15 MHz) for *N*-nitroso-derivatives (13) and (15) (probe temperature in $CDCl_3$) and for triazenes (11) and (12) (−80 °C in CS_2). The term $\Delta\nu$ is the internal difference in p.p.m. between the shifts of the ring carbons in position 2,6 ($\Delta\nu_{2,6}$) and 3,5 ($\Delta\nu_{3,5}$). Assignment has been made by analogy with that of ref. 20

Cmpd.	C-2	C-3	C-4	C-5	C-6	Me-2	Me-6	$\Delta\nu_{2,6}$	$\Delta\nu_{3,5}$
(13)	43.3	29.0	14.7	29.8	53.9	18.1	21.8	10.6	0.8
(15)	59.2	40.7	15.5	37.9	60.8	25.1	30.9	1.6	2.8
(11)	46.7	31.0	16.6	31.4	53.1	18.0	23.2	6.4	0.4
(12)	60.2	44.3	18.4	40.7	61.5	26.7	32.0	1.3	3.6

A lowering of $\Delta G^\ddagger$ with respect to unsubstituted piperidyl or non-cyclic alkyl derivatives had also been

* We could not check the effect on the 2- and 4-pyridyltriazines since the corresponding amines do not undergo diazotization, and cannot thus give the final products (see Experimental section).

† Both ring reversal and nitrogen inversion are conceivably faster [2,3,12,13] than the rotation about the N(1)–N(2) bond; we may thus consider the piperidyl ring as creating a ' virtual ' or ' dynamic ' plane, owing to the fast internal motions.

[9] L. Lunazzi, D. Macciantelli, and A. C. Boicelli, *Tetrahedron Letters*, 1975, 1205; L. Lunazzi, D. Macciantelli, G. Spunta, and A. Ticca, *J.C.S. Perkin II*, 1976, 1121.

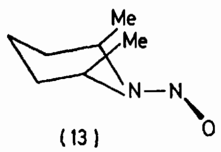
[10] L. Lunazzi, D. Macciantelli, and G. Cerioni, *J.C.S. Perkin II*, 1976, 1791.

[11] ' Dynamic N.m.r. Spectroscopy,' eds. L. M. Jackman and F. A. Cotton, Academic Press, New York, 1975.

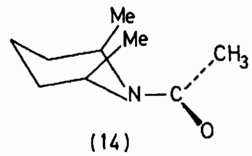
[12] J. B. Lambert, *Topics in Stereochem.*, 1971, **6**, 19; H. Booth, *Prog. in N.M.R. Spectroscopy*, 1969, **5**, 149.

[13] F. A. L. Anet, I. Yavari, I. J. Ferguson, A. R. Katritzky, M. Moreno-Manas, and M. J. T. Robinson, *J.C.S. Chem. Comm.*, 1976, 399. F. A. L. Anet and I. Yavari, *J. Amer. Chem. Soc.*, 1977, 2794.

observed in molecules similar to triazene (11), *e.g.* the N-nitrosoamine (13) and the amide (14).[2,14-17]



(13)



(14)

To rationalize this result, it was suggested [14,16,17] that the two 2,6-*cis*-methyl groups on the piperidyl ring adopt a diaxial conformation.

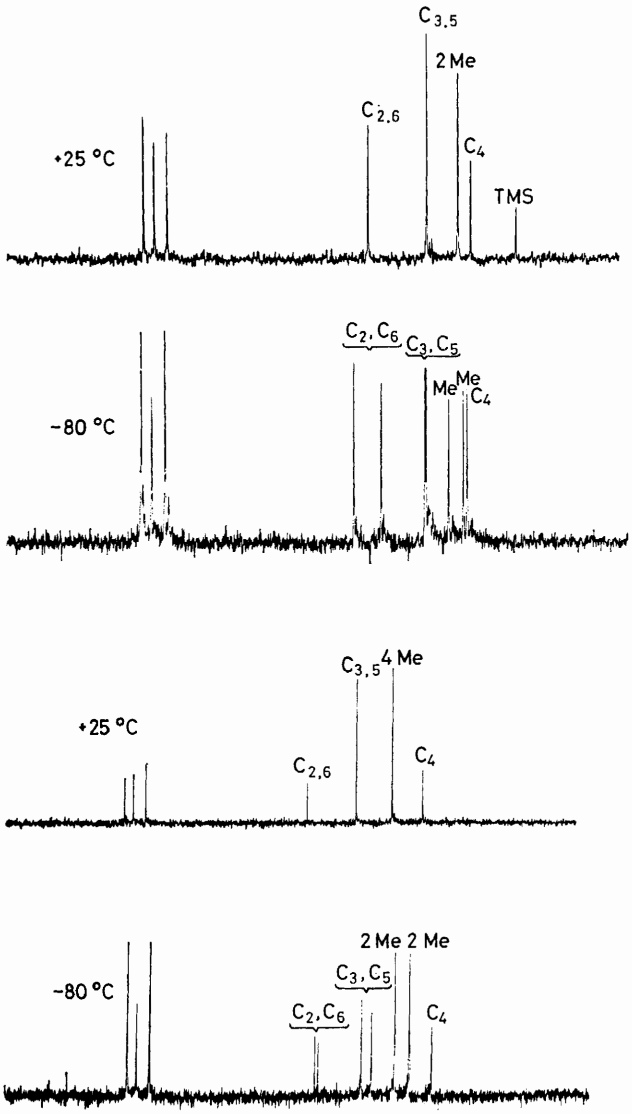
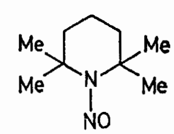


FIGURE 2 25.15 MHz ^{13}C spectra of derivatives (11) (upper two traces) and (12) (lower two traces) at 25 and −80 °C. The aromatic signals have not been assigned

It was also suggested that the axial–axial repulsion of these methyl groups (estimated [14,17] as 4—5 kcal mol^{-1}) was smaller than the repulsion (usually indicated [14,16] as $A^{1,3}$ strain) between the equatorial methyl groups and the substituent (*i.e.* –NO or –COMe); the latter was kept in the ' coplanar ' conformation by the driving force [14] of its partial double bond with the piperidyl nitrogen. The lowering of the rotational barrier in the 2,6-*cis*-dimethylpiperidyl-derivatives (13) and (14) with respect to their N-nitrosoamine or amide counterparts was thus attributed to the destabilization of the ground state, owing to the axial–axial repulsion of the two methyl groups.

A number of independent measurements [18-20] seems to support the diaxial *vs.* the diequatorial conformation. This model could be, in principle, extended to triazene (11), and would account for the lowering of its barrier with respect to the analogous noncyclic isopropyl derivative (3) ($\Delta\Delta G^\ddagger$ 3.6 kcal mol^{-1}).

However, this model seems to require, as a logical consequence, that the 2,2,6,6-tetramethylpiperidyl (TMP) derivatives with substituents in ' planar ' conformations, have an even smaller rotational barrier.* For, in addition to the repulsion of the two axial methyl groups, they cannot avoid the $A^{1,3}$ strain between the substituent and the equatorial methyl groups. On the contrary, we first showed [2] that the rotational barrier of the ' coplanar ' [3] N-nitroso-2,2,6,6-tetramethylpiperidine (15) is equal to that of the *cis*-DMP analogue (13); this observation is confirmed in the present work for triazenes, since the rotational barriers ($\Delta G^\ddagger$) of (11) and (12) are equal (Table 1).



(15)

Any further discussion upon the barriers in the TMP derivatives (12) and (15) thus requires an unambiguous proof that the *cis*-DMP derivatives (11), (13), and (14) really do have the two methyl groups in a diaxial conformation. Since none of them had been studied by X-ray diffraction, we decided to determine the structure of (11), and unambiguously established that the **2** methyl groups are *cis* and diaxial.

It has also been observed that the two axial methyl

* This argument obviously does not apply to those molecules (like hydrazones [2,3] and some imides [21]) where the substituent adopts a ' perpendicular ' conformation.

[14] Y. L. Chow, C. J. Colón, and J. N. S. Tam, *Canad. J. Chem.*, 1968, **46**, 2821.

[15] J. D. Cooney, S. K. Brownstein, and J. W. ApSimon, *Canad. J. Chem.*, 1974, **52**, 1974.

[16] R. R. Fraser and T. B. Grindley, *Tetrahedron Letters*, 1974, 4169.

[17] R. R. Fraser, T. B. Grindley, and S. Passananti, *Canad. J. Chem.*, 1975, **53**, 2473.

[18] T. P. Forrest, D. L. Hooper, and S. Ray, *J. Amer. Chem. Soc.*, 1974, **96**, 4286.

[19] G. E. Ellis, R. G. Jones, and M. G. Papadopulous, *J.C.S. Perkin II*, 1974, 1381.

[20] R. F. Fraser and T. B. Grindley, *Canad. J. Chem.*, 1975, **53**, 2465.

[21] L. Lunazzi, A. Dondoni, D. Tassi, and D. Macciantelli, to be published.

groups are slightly splayed apart in that whereas (see Figure 3 for crystallographic numbering) C(4)–C(8) is 2.55_5 Å, that of C(15)–C(16) is 3.449 Å.

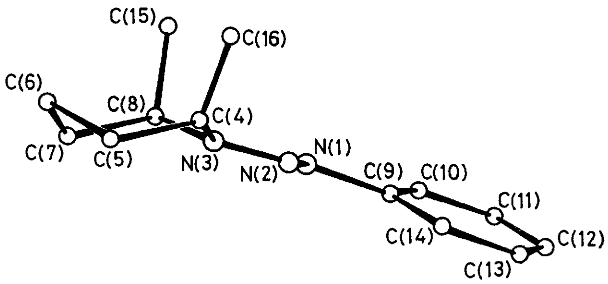


FIGURE 3 The structure of derivative (11), as determined by X-ray diffraction; hydrogen atoms are omitted. The molecule is projected along the *a* axis

Furthermore it was confirmed that the –N–N=N– group is ' coplanar ' with the DMP ring, as indicated by the ^{13}C experiment for solution: the plane of the N–N=N moiety and the plane of symmetry of the DMP ring are almost orthogonal (94.8°). Therefore the –N–N=N group is only 4.8° from perfect coplanarity with the mean plane created by the dynamic motion of the piperidyl ring.

The plane of the benzene ring is tilted by 10.5° with respect to the –N–N=N plane and by 15.5° with respect to the plane C(4),N(3),C(8) (Figure 3).

The *trans*-configuration of the azo-group has been also demonstrated and the preferred conformation, among the possible arrangements due to ring reversal and nitrogen inversion, determined (Figure 3). Crystallographic data are listed in Tables 3—5.

TABLE 3

Interatomic bond lengths (Å) of derivative (11), with estimated standard deviations in parentheses; crystallographic numbering is shown in Figure 3

N(1)–N(2)	1.259(7)	C(7)–C(8)	1.518)10)
N(1)–C(9)	1.421(7)	C(8)–C(15)	1.510(11)
N(2)–N(3)	1.338(7)	C(9)–C(10)	1.390(8)
N(2)–N(4)	1.455(8)	C(9)–C(14)	1.405(9)
N(3)–C(8)	1.451(8)	C(10)–C(11)	1.373(9)
C(4)–C(5)	1.504(13)	C(11)–C(12)	1.369(10)
C(4)–C(16)	1.516(13)	C(12)–C(13)	1.368(9)
C(5)–C(16)	1.521(11)	C(13)–C(14)	1.378(10)
C(6)–C(7)	1.508(10)		

TABLE 4

Bond angles (°) for derivative (11), with estimated standard deviations in parentheses

N(2)–N(1)–C(9)	112.5(5)	N(3)–C(8)–C(7)	109.9(5)
N(1)–N(2)–N(3)	114.4(5)	N(3)–C(8)–C(15)	112.0(6)
N(2)–N(3)–C(4)	112.9(5)	C(7)–C(8)–C(15)	113.2(6)
N(2)–N(3)–C(8)	122.6(4)	N(1)–C(9)–C(15)	115.1(5)
C(4)–N(3)–C(8)	123.2(5)	N(1)–C(9)–C(14)	126.0(5)
N(3)–C(4)–C(5)	110.3(6)	C(10)–C(9)–C(14)	118.9(6)
N(3)–C(4)–C(16)	111.5(6)	C(9)–C(10)–C(11)	120.1(6)
C(5)–C(4)–C(16)	114.1(7)	C(10)–C(11)–C(12)	121.0(6)
C(4)–C(5)–C(6)	113.4(6)	C(11)–C(12)–C(13)	119.5(6)
C(5)–C(6)–C(7)	108.2(6)	C(12)–C(13)–C(14)	121.3(7)
C(6)–C(7)–C(8)	113.2(7)	C(9)–C(14)–C(13)	119.2(6)

From consideration of these results the only possible explanation for a $\Delta(\Delta G^{\ddagger})$ 0 for (11) and (13) with respect to (12) and (15) is a nonchair conformation for the TMP ring in (12) and (15), since, if the TMP ring is in a twisted conformation, both the axial–axial repulsion and the $A^{1,3}$ strain can be released, and the ground state can become more stable than in the chair conformation.

TABLE 5

Relevant torsion angles (°) for derivative (11)

C(9)–N(1)–N(2)–N(3)	–175.6
N(2)–N(1)–C(9)–C(10)	–171.6
N(2)–N(1)–C(9)–C(14)	7.5
N(1)–N(2)–N(2)–C(4)	–170.4
N(1)–N(2)–N(3)–C(8)	–2.8
N(2)–N(3)–C(4)–C(5)	–151.5
N(2)–N(3)–C(4)–C(16)	80.8
C(8)–N(3)–C(4)–C(5)	41.1
C(8)–N(3)–C(4)–C(16)	–86.7
N(2)–N(3)–C(8)–C(17)	152.5
N(2)–N(3)–C(8)–C(15)	–80.8
C(4)–N(3)–C(8)–C(7)	–41.3
C(4)–N(3)–C(8)–C(15)	85.5
N(3)–C(4)–C(5)–C(6)	–47.6
C(16)–C(4)–C(5)–C(6)	78.7
C(4)–C(5)–C(6)–C(7)	57.7
C(5)–C(6)–C(7)–C(8)	–58.1
C(6)–C(7)–C(8)–N(3)	48.6
C(6)–C(7)–C(8)–C(15)	–77.6

The most likely twisted conformation is that shown in Figure 4 in which all the interactions are minimized.[22]

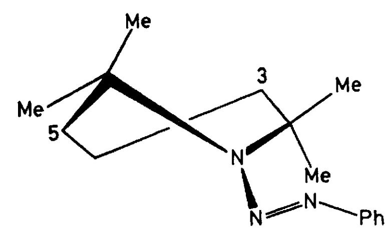


FIGURE 4 Proposed non-chair conformation for the 2,2,6,6-tetramethylpiperidyltriazene (12)

A consequence one would expect for the twisted arrangement we have suggested is that the environments of carbons 2 and 6 are much different from those experienced by the same carbons in a chair. The same is true of carbons 3 and 5.

The relative ^{13}C shifts of C-2 with respect to C-6 $(\Delta\nu_{2,6})$ and of C-3 with respect to C-5 $(\Delta\nu_{3,5})$ in (12) should therefore differ from the corresponding values in the derivative (11) which has a chair conformation.

Indeed the variations of these $\Delta\nu$ values in (12) with respect to those for (11) were found to be so large (Table 2) that they can be only explained by a substantial change in the molecular conformation. Analogous deviations have been reported,[20] and confirmed in the present work, for (15) with respect to (13) (Table 2).

Although anomalous ^{13}C shifts (*i.e.* ν values) cannot be considered sufficient evidence for non-chair conformations, we are here in the favourable situation of being

[22] D. J. Loomes and M. J. T. Robinson, *Tetrahedron*, 1977, **33**, 1149.

able to measure a difference of chemical shift (*i.e.* $\Delta\nu$) between pairs of diastereotopic carbons in a chair and in a seemingly twisted conformation. Under these circumstances variations of $\Delta\nu$ can be considered much better proof of conformational changes.

We may thus conclude that the combined evidence of the invariance of $\Delta G^{\ddagger}$ values and of the dramatic modification of $\Delta\nu_{2,6}$ and $\Delta\nu_{3,5}$, makes the TMP triazenes (12) and *N*-nitrosoamine (15) likely candidates to add to the list of non-chair conformers,[22-25] at least for solution.

EXPERIMENTAL

Preparation of Compounds.—The 1,1-dialkyl-3-aryltriazenes (1)—(12) were obtained by coupling the diazonium salts of the appropriate aromatic amines with various dialkylamines.[5,26] A typical preparation is described for triazene (11).

To a 5N-solution of hydrochloric acid (11 ml) was added aniline (4 g); the solution was then cooled to 0 °C and $NaNO_2$ (3.5 g) added dropwise. The resulting diazonium salt was added to 2,6-*cis*-dimethylpiperidine (3.9 g, Fluka), and aqueous Na_2CO_3 added until pH 9. The reaction mixture was then stirred (20 min), extracted with ether, dried (Na_2SO_4), distilled under vacuum (120—121 °C; 5 mmHg), and then crystallized (3.5 g) from methanol. Physical data of the new triazenes are: (2), b.p. 95—96° at 6 mmHg; (3), m.p. 38—39°; (4), b.p. 87° at 6 mmHg; (5), b.p. 112° at 7 mmHg; (6), m.p. 37—39°; (7) m.p. 43—44°; (8), m.p. 68—70°; (9), m.p. 53—54°; (10), m.p. 52—53°; (11), m.p. 40—41°; (12), m.p. 63—64°.

All solid products were crystallized from methanol or ethanol, and each had the expected molecular weight (mass spectrometry) and n.m.r. spectrum.

N.m.r. Spectra.—The proton spectra (in CS_2) were obtained with a JEOL C-60 HL equipped with a standard variable-temperature device. The temperature was monitored before or after each scanning by means of a thermocouple in a dummy tube.

The ^{13}C spectra were recorded with a JEOL PS 100 operating at 25.15 MHz in the Fourier-transform mode. Assignments of CH_3, CH_2, CH and quaternary carbons were obtained by means of ' off-resonance ' experiments.

The $\Delta G^{\ddagger}$ values for (11) and (12) were also determined at the coalescence point of the ^{13}C signals by taking advantage of the different pairs of non-equivalent carbons; free energies of activation were found in agreement with the t.l.s. determinations from the proton spectra, within 0.2 kcal mol^{-1}.

X-*Ray Diffraction.*—Single-crystal intensity data for derivative (11) were collected by use of an automatic Philips PW 1000 diffractometer and Mo-K_α radiation. Of 1 326 reflections measured, 538 were considered unobserved having $I < 3.5\sigma(I)$.

Crystal Data.—$C_{13}H_{19}N_3$, orthorhombic, $M = 217.1$, $a = 12.940(3)$, $b = 9.343(2)$, $c = 10.615(2)$ Å, $U = 1\,283.3$ Å^3, $Z = 4$, $D_c = 1.12$ g cm^3. Space group = $Pna2_1$. Mo-K_α radiation, $\lambda = 0.7107$ Å.

The structure was solved by direct methods by use of the SHELX program system.[27] All non-hydrogen atoms were located on the best Fourier map. Hydrogen atoms were positioned geometrically (assuming C–H 1.08 Å) and constrained for refinement, riding on their respective carbon atoms.

Overall isotropic temperature factors were refined for ring and for methyl hydrogen atoms, final values being 0.103 and 0.153 Å^2.

The final value of the agreement factor was 0.048. The weighting scheme was $w = 1/(\sigma F_o + 0.004F_o^2)$.

Atom co-ordinates, and their related thermal parameters are listed in Supplementary Publication No. SUP 22210 (8 pp., 1 microfiche).*

We thank the Consiglio Nazionale delle Ricerche (Rome) for financial support (to L. L.) and Dr. K. U. Ingold (Ottawa) for helpful discussion which were made possible by the N.A.T.O. Research Grants Programme. We also thank Professor P. F. Zanazzi, University of Perugia, for collecting reflection data for compound (11).

[7/947 *Received, 2nd June,* 1977]

* See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1977, Index issue.

[23] G. M. Kellie and F. G. Riddell, *J. Chem. Soc. (B)*, 1971, 1030; G. Ellis and R. C. Jones, *J.C.S. Perkin II*, 1972, 437.

[24] N. K. Wilson and J. B. Stothers, *Topics in Stereochem.*, 1974, **8**, 56.

[25] G. M. Kellie and F. G. Riddell, *Topics in Stereochem.*, 1974, **8**, 225.

[26] C. S. Rondestvedt, jun., and S. J. Davis, *J. Org. Chem.*, 1957, **22**, 200.

[27] G. M. Sheldrick, SHELX: A program for Crystal Structure Determination, University Chemical Laboratory, Cambridge.