ELSEVIER

Journal of Fluorine Chemistry 113 (2002) 51–53

JOURNAL OF FLUORINE CHEMISTRY

www.elsevier.com/locate/jfluchem

The molecular configuration of bis(trifluoromethyl)nitroxide $(CF_3)_2NO^\bullet$

Christopher J. Rhodes[a,*], Chantal S. Hinds[a], C. Alan Heaton[a], Richard L. Powell[b], R. Eric Banks[b], Basil T. Abdo[b], Steven Rogers[c]

[a]*School of Pharmacy and Chemistry, Liverpool John Moores University, Byrom St., Liverpool L3 3AF, UK*
[b]*Department of Chemistry, UMIST, P.O. Box 88, Manchester M60 IQD, UK*
[c]*ICI Ltd., Wilton Centre, P.O. Box 90, Wilton, Middlesborough, Cleveland TS90 8J, UK*

Received 14 March 2001; accepted 6 July 2001

Abstract

Anisotropic ^{14}N couplings have been determined using electron paramagnetic resonance spectroscopy for the radicals, bis(trifluoromethyl)nitroxide and di-*tert*-butylnitroxide as isolated in a polycrystalline fluorotrichloromethane matrix at 77 K. The results show that the nitrogen $2p_z$ orbital spin-population in bis(trifluoromethyl)nitroxide is 26%, as compared with 48% in di-*tert*-butylnitroxide, which is due mainly to the importance of the oxygen-localised canonical structure $(CF_3)_2N–O–$ and to spin-delocalisation onto the CF_3 groups: it is the large oxygen atom spin density of 0.63 that determines the relatively high reactivity of bis(trifluoromethyl)nitroxide in hydrogen-atom transfer reactions. On the basis of their anisotropic and isotropic ^{14}N couplings (measured in liquid fluorotrichloromethane), it is concluded that the configuration at the nitrogen centre is near-planar in both nitroxides. This result is supported by molecular orbital calculations made on these, and related molecules in order to evaluate some of the theoretical methods available to organic chemists. © 2002 Published by Elsevier Science B.V.

Keywords: Bis(trifluoromethyl)nitroxide; Di-*tert*-butylnitroxide; Electron paramagnetic resonance; Spin density; Reactivity

1. Introduction

Bis(trifluoromethyl)nitroxide, $(CF_3)_2NO$, [1] is one of the most reactive nitroxides known, and detailed measurements have been made of its kinetic [2] and physical [3,4] properties. EPR studies [1,3] of the radical in liquid solution show that the isotropic ^{17}O coupling is raised (23.6 G) [3] compared to di-*tert*-butylnitroxide, $(Me_3C)_2NO$ (19.4 G) [3], in accordance with an increased weighting of the canonical structure $(CF_3)_2N–O^\bullet$. The isotropic $a(^{14}N)$ coupling is concomitantly reduced (8.3 G cf. 13.7 G), but since the ratios of $a(^{14}N)$ and $a(^{17}O)$ couplings for the two radicals do not correspond with a simple shift of spin density from nitrogen to oxygen, further delocalisation onto the CF_3 groups must be considered. To explore the feature of spin density distribution between the different constituents of these molecules, we undertook an EPR study of them as isolated in a solid matrix at 77 K, since this reveals directly the p-orbital population at a nitrogen atom through the manifestation of the ^{14}N anisotropic (dipolar) coupling. This does not appear to have been done previously for $(CF_3)_2NO^\bullet$. The results are compared with those for di-*tert*-butylnitroxide, $(Me_3C)_2NO^\bullet$.

2. Results and discussion

2.1. EPR measurements

A direct determination of orbital spin populations is possible from the measurement of anisotropic hyperfine couplings from radicals which are immobilised in solid cryogenic matrices: we chose $CFCl_3$ as the matrix material since bis(trifluoromethyl)nitroxide does not react with it [1], and it is well established to provide a highly rigid medium at 77 K, for instance in studies of reactive organic radical cations [5]. The EPR data are listed in Table 1, which include an anisotropic (parallel) coupling of 18.8 G for bis(trifluoromethyl)nitroxide, from which the dipolar contribution (10.5 G) may be estimated by subtraction of the isotropic coupling (8.3 G) measured in liquid $CFCl_3$ solution at 293 K. This leads to a nitrogen $2p_z$ population of 0.26 (taking $2B_0 = 39.66$ G [6]), which may be compared with that (0.48) determined similarly for di-*tert*-butylnitroxide.

---

[*] Corresponding author.
E-mail address: c.rhodes@livjm.ac.uk (C.J. Rhodes).

0022-1139/02/$ – see front matter © 2002 Published by Elsevier Science B.V.
PII: S0022-1139(01)00466-3

Table 1
EPR hyperfine coupling constants ($G = 10^{-4}$ T) for nitroxide radicals

Radical	Couplings	T (K)
$(CF_3)_2NO^\bullet$	$a(^{19}F)9.3$, $a(^{14}N)8.3$	293
	$a(^{19}F)9.0$, $a_{\parallel}(^{14}N)18.8$	77
$(Me_3C)_2NO^\bullet$	$a(^{14}N)13.7$	293
	$a_{\parallel}(^{14}N)32.6$	77

Taking the sum of the oxygen $2p_z$ and nitrogen $2p_z$ spin populations to be unity, an oxygen $2p_z$ population of 0.52 is deduced for di-*tert*-butylnitroxide, which is reflected in the ^{17}O isotropic coupling constant of 19.4 G [3], therefore, the oxygen $2p_z$ spin population in bis(trifluoromethyl)nitroxide, according to its 23.6 G isotropic ^{17}O coupling [3], is 0.63, and since the spin population of the N $2p_z$ orbital is 0.26, we conclude that the remaining 11% of the spin density is delocalised onto the CF_3 groups.

We do not observe hyperfine resolution on the perpendicular feature in either nitroxide studied here, and for this reason have used the isotropic (solution) $a(^{14}N)$ couplings along with the parallel ^{14}N couplings to determine the p/s orbital hybridisation state for the nitrogen atoms. This amounts to 22.4 in di-*tert*-butylnitroxide and 21.1 in bis(trifluoromethyl)nitroxide, which is essentially as expected for π-radicals; i.e. both can deviate only slightly from planarity at the nitrogen atom, but any such deviation is largest in bis(trifluoromethyl)nitroxide. We note that the p/s ratio for an idealised tetrahedral configuration would be 3.0.

2.2. Relationship between spin distribution and reactivity for bis(trifluoromethyl)nitroxide and tert-butylperoxyl radicals

Doba and Ingold [2] have pointed out that the absolute reactivities of bis(trifluoromethyl)nitroxide and *tert*-butylperoxyl radicals are essentially identical in H-atom transfer (abstraction) reactions at ambient temperatures (i.e. the isokinetic temperature); this is reflected in the similar O–H bond strengths for the compounds $(CF_3)_2NO{-}H$ (85.3 ± 3.0) and $Me_3COO{-}H$ (88.5 ± 1.5 kcal/mol), the former being raised considerably from that in dialkyl nitroxides [3] (ca. 70 kcal/mol). Sevilla and co-workers [7] have reported correlations between the reactivities of peroxyl radicals and the parallel ^{17}O couplings which reflect the spin density at the terminal oxygen atom, $ROO^\bullet$. In this regard, we note that our estimate for the O $2p_z$ population in bis(trifluoromethyl)nitroxide of 0.63 is almost identical with that in *tert*-butylperoxyl (0.62), and so we conclude that it is the frontier orbital $ROO^\bullet$ spin population which determines the reactivities of nitroxide and peroxyl radicals toward H-atom abstraction reactions, i.e. the total oxyl radical character $X{-}O^\bullet$, not only the relative contribution of structures (1)/(2) and (3)/(4) since the ratio of $^{17}O/^{14}N$; $^{17}O/^{17}O$ $2p_z$ spin populations are quite disparate [2.42 and 1.59, respectively in $(CF_3)_2N{-}O^\bullet$ and $Me_3COO^\bullet$].

$$\underset{(1)}{R_2N{-}O^\bullet} \leftrightarrow \underset{(2)}{R_2N^{+\bullet}{-}O^-} \qquad \underset{(3)}{ROO^\bullet} \leftrightarrow \underset{(4)}{RO^{+\bullet}{-}O^-}$$

2.3. Calculations of the configurations of nitroxide radicals and related molecules

Nitroxide radicals, (1)/(2), should be planar if the principal factor in determining the geometry at nitrogen is maximising the mixing of the nitrogen lone-pair orbital with the oxygen orbital containing the single electron. Maximum overlap and thus mixing of these orbitals is achieved if the two carbon atoms and the oxygen attached to the nitrogen are co-planar. However, this simple approach omits possible energy-increasing changes elsewhere in the structure of the molecule which might be necessary to accommodate planarity at nitrogen. We have therefore calculated the geometries of dimethylnitroxide radicals by ab initio and semi-empirical methods, to compare with our results on this issue from EPR spectroscopy.

3. Conclusions

The improper torsion angle (γ) is a useful way of estimating how closely the geometries of the compounds in Tables 2–4 approach planarity. For a planar molecule,

Table 2
Key bond lengths and bond angles from PM3 semi-empirical calculations for the compounds shown

Compound	C–N–C (°)	C–N–O (°)	γ (°)	N–O (Å)	C–N (Å)
$(CH_3)_2NO^\bullet$	115.4	121.9	169.3	1.248	1.484
$(CF_3)_2NO^\bullet$	113.5	121.8	158.1	1.236	1.536
$(CF_3)_2NO^-$	104.7	112.4	122.3	1.263	1.589
$(CF_3)_2NOH$	114.8	109.8	124.2	1.436	1.508

Table 3
Key bond lengths and bond angles from AM1 semi-empirical calculations for the compounds shown

Compound	C–N–C (°)	C–N–O (°)	γ (°)	N–O (Å)	C–N (Å)
$(CH_3)_2NO^\bullet$	115.0	119.9	154.6	1.218	1.460
$(CF_3)_2NO^\bullet$	114.3	118.3	146.6	1.198	1.553
$(CF_3)_2NO^-$	101.9	111.3	118.7	1.191	1.652
$(CF_3)_2NOH$	111.9	108.8	120.2	1.324	1.535

Table 4
Key bond lengths and bond angles from an ab initio calculations for $(CH_3)_2NO$

	C–N–C (°)	C–N–O (°)	γ (°)	N–O (Å)	C–N (Å)
$(CH_3)_2NO^\bullet$	118.4	116.9	148.2	1.263	1.448

γ will be 180°, while a tetrahedral molecule will have a value of 120°. All three calculational methods clearly predict that dimethylnitroxide will not be perfectly planar although it is estimated to be closer to planarity than bis(trifluoromethyl)-nitroxide (this accords with the p/s hybridisation ratios for the nitrogen atom determined by EPR for di-*tert*-butylnitroxide and bis(trifluoromethyl)nitroxide); however, since the bond angles at the nitrogen centre sum to >350° in both cases for all calculations, the degree of bending is not large, as the EPR results further show. The radical bis(trifluoromethyl)-nitroxide is predicted by both methods to be more planar than the related anion, $(CF_3)_2NO^-$ and the parent hydroxylamine, $(CF_3)_2NOH$.

The older AM1 method, as opposed to its later development PM3, based on a wider range of data, is in closer agreement with the ab initio method regarding the predicted bond angle values for dimethylnitroxide. Both AM1 and PM3 are in reasonable agreement with ab initio regarding bond lengths. Most importantly, PM3 predicts the most nearly planar nitrogen centres for both the dialkyl and bis(perfluoroalkyl) nitroxides, and may be taken to accord most closely with the experimental result.

4. Experimental

Bis(trifluoromethyl)nitroxide was prepared as described previously [8], except that potassium permanganate was used instead of silver(II) oxide to oxidise *N*,*N*-bis(trifluoromethyl)hydroxylamine, and was dissolved in $CFCl_3$, at a concentration of 1.0 wt.%. The solution was deoxygenated via. freeze–pump–thaw cycles in a silica tube which was sealed and then transferred to an insert Dewar supported in the cavity of an EPR spectrometer (Bruker ER200D). Di-*tert*-butylnitroxide (Aldrich) was treated similarly. For the 77 K measurement, the sample was frozen by adding liquid nitrogen to the Dewar vessel; after warming to ambient temperature, a spectrum was recorded identical with that recorded originally at room temperature, showing that the changes in the spectrum incurred by freezing were not due to any chemical alteration of the sample, but were entirely those of immobilisation of the nitroxide on the timescale for EPR observation.

Semi-empirical calculations were performed using the versions of AM1 and PM3 included in the ‘‘Hyperchem’’ package. An ab initio calculation on the dimethylnitroxide radical used a UMP2/sv 6-3IG** basis set. Tables 2 and 3 summarise the results from the semi-empirical calculations in the form of key bond lengths and angles. Corresponding values for related non-radical anions and hydroxylamines were also calculated to provide comparisons. The ab initio results for $Me_2NO^\bullet$ are given in Table 4.

References

[1] R.E. Banks, in: R.E. Banks, M.G. Barlow (Eds.), Fluorocarbon and Related Chemistry, Specialist Periodic Reports, The Chemical Society, London, Vol. 1, 1971, p. 109; Vol. 2, 1974, p. 223; Vol. 3, 1976, p. 235.
[2] T. Doba, K.U. Ingold, J. Am. Chem. Soc. 106 (1984) 3958.
[3] C. Chatgilialoglu, V. Malatesta, K.U. Ingold, J. Phys. Chem. 84 (1980) 3597.
[4] D.A.C. Compton, C. Chatgilialoglu, H.H. Mantsch, K.U. Ingold, J. Phys. Chem. 85 (1981) 3093.
[5] C.J. Rhodes, in: M.C.R. Symons (Ed.), Electron Spin Resonance, Specialist Periodical Reports, The Royal Society of Chemistry, Cambridge, Vol. 13A, 1992, p. 56.
[6] J.R. Morton, K.F. Preston, J. Magn. Reson. 30 (1978) 577.
[7] M.D. Sevilla, D. Becker, M. Yan, J. Chem. Soc. Faraday Trans. 86 (1990) 3279.
[8] R.E. Banks, C. Oppenheim, J. Fluorine Chem. 12 (1978) 27.