Nitrogen Nuclear Magnetic Resonance Spectroscopy. Part V.[1] Diazirine, Diazomethane, and Related Azo-, Diazo-, and Tetra-azo-compounds, some Comments on Dinitrogen as a Ligand, and an Improved Absolute Scale for Nitrogen Shielding

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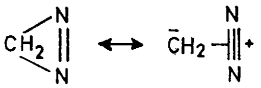
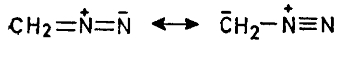
Nitrogen-14 n.m.r. measurements of diazirine, diazomethane, diphenyldiazomethane, ethyl diazoacetate, tetramethyl- and tetraethyl-tetraz-2-ene, and diethyl azodicarboxylate are reported. The diamagnetic and paramagnetic shielding of the two nitrogens in diazomethane is compared with that of central and terminal nitrogen in other linear triatomic systems [OCN, CNC (isocyano), NNN, NCN (carbodi-imide), and CCN], and carbon in allene (C=C=C). The nitrogen shielding is higher in the CH_2N_2 isomers than in unstrained *cis*- or *trans*-diazo-compounds, and for diazirine and molecular N_2 it is intermediate between that of the diazomethane nitrogens. These compounds help to define regions in which the absorption of dinitrogen ligands might be expected. The ^{15}N resonances assigned by Bercaw to edge-on and end-on co-ordinated dinitrogen in $[Ti(C_5Me_5)_2(N_2)]$ are significantly downfield of the region expected for these, and are in (and downfield of) the region of azo-nitrogen (X–N=N–X). An absolute scale for nitrogen shielding is appended, based on DeLucia and Gordy's accurate molecular-beam maser measurement of the spin-rotation constants in NH_3, combined with Alei's chemical-shift measurements for $^{15}NH_3$(g) relative to $[^{15}NH_4]^+$(aq).

We report ^{14}N n.m.r. measurements of the CH_2N_2 isomers, diazirine (I) and diazomethane (II), and of related azo-, diazo-, and tetra-azo-compounds. Although it was not made until 1960,[2] diazirine has the three-membered ring structure that was used by Curtius [3] to describe the aliphatic diazo-group, until the Angeli–Thiele linear structure [4,5] gained ground against its handicap of an unusual valence formulation. The possibility of edge-on as well as end-on attachment of

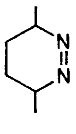


(I)

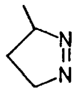


$$\overset{-}{C}H_2=\overset{+}{N}=\overset{-}{N} \longleftrightarrow \overset{-}{C}H_2-\overset{+}{N}\equiv N$$

(II)



(III)



(IV)

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[1] Part IV, J. Mason and W. van Bronswijk, *J. Chem. Soc.* (*A*), 1971, 791.

[2] E. Schmitz, *Angew. Chem. Internat. Edn.*, 1964, **3**, 333 and references therein.

[3] T. Curtius, *Chem. Ber.*, 1883, **16**, 754.

[4] A. Angeli, *Atti Accad. naz. Lincei. Rend. Classe Sci. fis. mat. nat.*, 1907, **16**, 790.

[5] J. Thiele, *Chem. Ber.*, 1911, **44**, 2522.

the dinitrogen ligand in metal complexes[6] prompts a comparison of the CH_2N_2 isomers in corresponding terms.

RESULTS AND DISCUSSION

Diazirine and Azo-compounds.—Table 1 compares the nitrogen shift in diazirine with those measured for open-chain azo- and tetrazo-compounds, which are all *trans* except for *cis*-$F_3CN{:}NCF_3$. Also given are the wavelengths of the low-energy $n\rightarrow\pi^*$ bands. In nitroso-compounds[7] the nitrogen shifts follow the $n\rightarrow\pi^*$ inverse energies, the atomic $p_x\rightarrow p_y$ component of the excitation being magnetic-dipole allowed, though electric-dipole forbidden. In the azo-group the n orbitals are split into two molecular orbitals (m.o.s), one bonding (n_n) and one antibonding (n_a); the longer-wavelength transition, from the higher of these, is allowed in *cis* compounds, forbidden in *trans*, but magnetic-dipole allowed in both. The variation of the nitrogen shielding with the $n\rightarrow\pi^*$ wavelength is less marked than for the nitroso-compounds but still evident, and this correlation is now extended in Table 1. In the *trans* compounds, XN:NX, the nitrogen line tends to move upfield with blue-shifting of the $n\rightarrow\pi^*$ band, as the electronegativity of the ligand X increases thus stabilising the n relative to the π^* orbital, and also as π-electron release by the ligand ($R < F < OH < NR_2$) raises the π^* orbital. The line moves downfield if the ligand (*e.g.* CO_2Et) stabilises the π^* relative to the n orbital.

TABLE 1

Nitrogen shifts in azo-compounds, compared with the inverse energy of the $n_a\rightarrow\pi^*$ band. The u.v. measurements refer to the gas unless a solvent is given

Compound		δ [a]/p.p.m.	Width [b]/Hz	Ref.	$n_a\rightarrow\pi^*$ band $\lambda_{max.}$/nm	 ε/dm^3 mol^{-1} cm^{-1}	Ref.
$\overline{CH_2{-}N{=}N}$ (ether)		308 (6)	61		308	176	*c*
$Et_2N{\cdot}N{:}N{\cdot}NEt_2$ (l)	=N–	323 (5)	525		*ca.* 280		*d*
	>N–	57 (7)	747				
cis-FN:NF (l)		360		8			
$Me_2N{\cdot}N{:}N{\cdot}NMe_2$ (l)	=N–	383 (5)	331		276	355	*e*
	>N–	116 (5)	496				
trans-FN:NF (l)		422		8			
HON:NOH (aq. acid)		439		1	243 (aq)	100(*infl.*)	*f*
cis-$F_3CN{:}NCF_3$ (l) [g]		493	160	1	355	2	
EtN:NEt (1)		505	260	1	355	10	9*c*
$EtO_2C{\cdot}N{:}N{\cdot}CO_2Et$ (ether)		518 (2)	320		405	40	*d*

[a] Chemical shift relative to $[NH_4]^+$(aq), downfield as positive. The numbers in parentheses are uncertainties in units of the last digit. [b] Linewidth at half-height, ±(5—10)%. [c] W. H. Graham, *J. Amer. Chem. Soc.*, 1962, **84**, 1063. [d] H. Bock, *Angew. Chem. Internat. Edn.*, 1965, **4**, 457. [e] G. Kortüm, *Z. phys. Chem.* (*Leipzig*), 1941, **B50**, 361. [f] M. N. Hughes and G. Stedman, *J. Chem. Soc.*, 1963, 1239; J. R. Buchholz and R. E. Powell, *J. Amer. Chem. Soc.*, 1963, **85**, 509. [g] *cf.* The electron-diffraction study of C. H. Chang, R. F. Porter, and S. H. Bauer, *J. Amer. Chem. Soc.*, 1970, **92**, 5313.

In related *cis* and *trans* azo-compounds the $n\rightarrow\pi^*$ energies are similar and the nitrogen shielding is likely to be so (*cf.* the 60 p.p.m. difference for *cis* and *trans* FN:NF[8]). The $n\rightarrow\pi^*$ band in unstrained azo-compounds is somewhat red-shifted from *trans* to *cis*,[9a] *e.g.* from 355 nm in azoethane to 382 in the tetrahydropyridazine derivative (III),[9b] and somewhat blue-shifted in a five-membered ring, *e.g.* to 324 nm in the pyrazoline (IV).[9c] The upfield shift of 200 p.p.m. from azoethane to diazirine may well be due to delocalisation of the n_a electrons in the three-membered ring. The important difference from a normal azo-compound, arising from the small CNN angle (65.5°) in diazirine, is that the n orbitals, pointing away from the ring, include carbon as well as nitrogen. *Ab initio* calculations[10a] with the n orbitals collinear with the CN bonds indicate that the n_a electrons are 40% on carbon in diazirine, and since the π^* orbital is wholly on nitrogen there is considerable electron transfer from carbon to nitrogen in the $n\rightarrow\pi^*$ transition. This suggests that the $n\rightarrow\pi^*$ circulation is not as close to nitrogen, *i.e.* deshields nitrogen less well, in diazirine compared with azo-groups. These calculations show some negative charge on carbon, but this is due to polarisation of the methylene group for there is little net charge on nitrogen. This conclusion is supported by ^{14}N nuclear quadrupole coupling studies of diazirine, but the computations of the ^{14}N electronic-field gradients support a bonding scheme with the n orbitals collinear with the NN bond.[10b]

Diazomethane and Related Compounds.—Two nitrogen lines of equal integrated intensity are given by the aliphatic diazo-compounds ethyl diazoacetate, diazomethane, and diphenyldiazomethane. (As in the ^1H n.m.r. study of diazomethane,[11a] there was no sign of the isodiazomethane tautomer HCNNH formerly thought to

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[6] J. E. Bercaw, E. Rosenberg, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1974, **96**, 612; J. E. Bercaw, *ibid.*, p. 5087.

[7] L.-O. Andersson, J. Mason, and W. van Bronswijk, *J. Chem. Soc.* (*A*), 1970, 296.

[8] Shifts for *cis*- and *trans*-FN:NF relative to NF_3 are from J. H. Noggle, J. D. Baldeschwieler, and C. B. Colburn, *J. Chem. Phys.*, 1962, **37**, 182. The NF_3 shift relative to $[NO_3]^-$(aq) is given by J. Mason and W. van Bronswijk, *Chem. Comm.*, 1969, 357.

[9] (*a*) R. F. Hutton and C. Steel, *J. Amer. Chem. Soc.*, 1964, **86**, 745; (*b*) S. G. Cohen and R. Zand, *ibid.*, 1962, **84**, 586; (*c*) M. B. Robin, R. R. Hart, and N. A. Kuebler, *ibid.*, 1967, **89**, 1564.

[10] (*a*) J. R. Lombardi, W. Klemperer, M. B. Robin, H. Basch, and N. A. Kuebler, *J. Chem. Phys.*, 1969, **51**, 33; M. B. Robin, H. Basch, N. A. Kuebler, K. B. Wiberg, and G. B. Ellison, *ibid.*, p. 45; (*b*) J. M. Pochan and W. H. Flygare, *J. Phys. Chem.*, 1972, **76**, 2249.

[11] (*a*) D. F. Koster and A. Danti, *J. Chem. Phys.*, 1964, **41**, 582; (*b*) W. H. Graham, *J. Amer. Chem. Soc.*, 1962, **84**, 1063.

be present.) The line at higher field for each molecule (Table 2) is the less affected by substitution and is assigned to terminal nitrogen, in agreement with the assignment of the nitrogen resonances in azide ion [12] and dinitrogen mono-oxide,[13] also given in Table 2, in which the terminal nitrogen resonates at higher field, and also with that of the carbon resonances in allene, $CH_2{=}C{=}CH_2$, in which the terminal and central carbons resonate respectively at 72.6 and 211.7 p.p.m. from $SiMe_4$.[14]

TABLE 2

Nitrogen shifts for molecules containing the linear groupings OCN, NNN, NNO, NCN, and CNN, together with the wavelengths of the magnetically active u.v.–visible bands (1) and (2), as described in the text

	Terminal nitrogen		U.v.–visible bands			Central nitrogen		
			$\lambda_{max.}$/nm					
Compound	δ [a]/p.p.m.	Width [b]/Hz	(1)	(2)	Ref.	δ [a]/p.p.m.	Width [b]/Hz	Ref.
$[OCN]^-$ (aq)	65	15	195	147	16			19*a*
$[N_3]^-$ (aq)	76	22	230	155	16	225	55	12
$H_{11}C_6{\cdot}N{:}C{:}N{\cdot}C_6H_{11}$	113		270		*c*			*d*
N_2O (l)	131		273	145	16	215		13
$EtO_2C{\cdot}CHNN$	245 (2)	67	353		*e*	336 (7)	600	
CH_2NN (ether)	265 (2)	20	400	190	15	369 (2)	80	
$Ph_2CNN(CH_2Cl_2)$	274 (2)	140	525		*f*	414	200	

[a] Chemical shift relative to $[NH_4]^+$(aq), downfield as positive; the numbers in parentheses are the uncertainties in units of the last digit. [b] Linewidth at half-height, ±(5—10)%. [c] G. C. Lardy, *J. Chim. phys.*, 1924, **21**, 281. [d] J. D. Ray, L. H. Piette, and D. P. Hollis, *J. Chem. Phys.*, 1958, **29**, 1022. [e] G. Kortüm, *Z. phys. Chem.* (*Leipzig*), 1941, **B50**, 361. [f] Dr. D. T. Eastlick, personal communication.

TABLE 3

Absolute shielding parameters for molecules containing linear OCN, CNC, NNN, NNO, CNN, and CCN groups, and some related molecules. The derivation of the parameters is given in the Appendix; $\langle r^{-3}\rangle_{2p}$ is measured in atomic units, and the shielding parameters in p.p.m.

	Terminal nitrogen					Central nitrogen				
Compound	$\langle r^{-3}\rangle_{2p}$	δ	σ_d	σ(δ)	σ_p	$\langle r^{-3}\rangle_{2p}$	δ	σ_d	σ(δ)	σ_p
$[OCN]^-$	2.09	65	408	155	−253					
MeNC						2.39	135	427	85	−342
$[N_3]^-$	2.08	76	418	144	−274	2.64	225	450	−5	−455
N_2O	2.39	131	414	89	−325	2.78	215	446	5	−441
MeCN		229	410	−9	−419					
CH_2NN	2.39	265	412	−41	−457	2.61	369	435	−149	−584
N_2	2.47	289 *	385	−69	−454					
$\overline{CH_2{-}N{=}N}$	2.42	308	426	−88	−514					

* Ref. 32*b*.

Table 2 also contains the wavelengths of the weak low-energy bands, (1), which for the diazo-compounds [15] probably arise from an excitation of the $\pi' \rightarrow \pi^*$ type (the π' orbitals lying in the molecular plane), and for $[N_3]^-$ and N_2O (also $[OCN]^-$) from the corresponding ${}^1\Sigma_g{}^+ \longrightarrow {}^1\Sigma_u{}^-$ and ${}^1\Sigma^+ \longrightarrow {}^1\Sigma^-$ excitations respectively, all these corresponding to the $n \rightarrow \pi^*$ transitions in azo-compounds. The $\sigma \rightarrow \pi^*$ transitions at shorter wavelengths are magnetically active also, and are listed under (2) for molecules for which (tentative) assignments of the bands are available.[16] For both the terminal and the central nitrogen, the line tends to move upfield as these bands move to shorter wavelengths.

In allene the lower-field resonance of the central carbon has been explained [17] as due to deshielding by two $\sigma \leftrightarrow \pi$ circulations, as opposed to one for the terminal carbon. Table 3 separates some factors involved in a comparison of the shielding of central (N_c) and terminal nitrogen (N_t) in the linear triatomic skeletons OCN, NNN, NNO, CNC, CNN, NCN, and CCN. The shielding parameters are molecular terms (as defined by Ramsey [18]) relative to the bare nucleus, with the nucleus of interest as origin, and their derivation is described in the Appendix together with that of the radial term $\langle r^{-3}\rangle_{2p}$. Table 3 shows that although the paramagnetic term σ_p is dominant as usual, the variation in the diamagnetic term σ_d is not negligible. The latter is about 30 p.p.m. larger for N_c, with two second-row ligands, than for N_t, with only one, so that the increase in $|\sigma_p|$ from N_t to N_c is up to 40% larger than would appear from the chemical shifts uncorrected for variation in σ_d.* The term σ_p increases

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* Similarly σ_p is 240 p.p.m. smaller in diazirine than in azomethane, since σ_d is 40 p.p.m. smaller (*cf.* the 200 p.p.m. difference in δ).

[12] W. Beck, W. Becker, K. F. Chew, W. Derbyshire, N. Logan, D. M. Revitt, and D. B. Sowerby, *J.C.S. Dalton*, 1972, 245 and references therein.

[13] J. E. Kent and E. L. Wagner, *J. Chem. Phys.*, 1966, **44**, 3530.

[14] J. K. Crandall and S. A. Sojka, *J. Amer. Chem. Soc.*, 1972, **94**, 5084; R. A. Friedel and L. Retcofsky, *ibid.*, 1963, **85**, 1300.

[15] R. K. Brinton and D. H. Volman, *J. Chem. Phys.*, 1951, **19**, 1394; G. Herzberg, *Proc. Roy. Soc.*, 1961, **A262**, 291; A. J. Merer, *Canad. J. Phys.*, 1964, **42**, 1242; J. Del Bene and H. H. Jaffe, *J. Chem. Phys.*, 1969, **50**, 1126.

[16] J. W. Rabalais, J. R. McDonald, V. Scherr, and S. P. McGlynn, *Chem. Rev.*, 1971, **71**, 93 and references therein.

[17] J. A. Pople, *Discuss. Faraday Soc.*, 1962, **34**, 7; *J. Chem. Phys.*, 1962, **37**, 53.

[18] N. F. Ramsey, *Phys. Rev.*, 1950, **78**, 699; 'Molecular Beams,' Oxford, 1956.

(becomes more negative) from N_t to N_c by 28% for CH_2N_2, by 35% for N_2O, and by 66% for $[N_3]^-$, but, as Table 3 shows, a significant part of this increase is in the radial term $\langle r^{-3}\rangle_{2p}$, which is large for 'allene-type' nitrogen, $=\overset{+}{N}=$ (and increased by an electronegative ligand as in N_2O). The radial term is large also for isocyano-type quaternary nitrogen, $-\overset{+}{N}\equiv$, as evidenced by the value for MeNC, but σ_p is then relatively small because of the cylindrical symmetry (*cf.* also N_c in $[N_3]^-$ and N_2O). The shielding thus provides evidence for the relative contributions of the allene- and isocyano-type structures to diazomethane, (II). As to the allene-type contribution, σ_p for N_t is 40 p.p.m. greater than in MeCN, but σ_p for N_c is 140 p.p.m. greater than in MeNC. Evidence for the contribution of the isocyano-form in diazomethane is given by the ^{13}C shielding in allene,[14] since the ratio of the σ_p values for N_c and N_t in CH_2NN, 1.28 : 1, is significantly smaller than the ratio of the values for C_c and C_t in allene, 1.65 : 1, and also by the proton shielding [11a] since the diazomethane protons resonate *ca.* 1 p.p.m. upfield of those in allenes and 2 p.p.m. upfield of those in ethene (and 1.1 p.p.m. downfield of the diazirine protons [11b]). CNDO–CI calculations on diazomethane indicate that N_c is positively charged, by *ca.* 0.4e, more than half this charge being lost to carbon: allene shows a corresponding but smaller charge separation.[15]

Diazirine, Diazomethane, and Dinitrogen.—The nitrogen line in diazirine, upfield of azo-nitrogen, is roughly midway between the lines for N_c and N_t in diazomethane, and this is true also of the corresponding σ_d and σ_p values (Table 3). Interestingly, in the comparison of dinitrogen with related ligands ($[N_3]^-$, $[CN]^-$, MeCN, CO, *etc.*), the resonance in molecular nitrogen is close to that in diazirine (*i.e.* between those for CH_2NN) just as the resonance for nitrogen (or carbon) bonded to carbon in the methyl derivatives of the related ligands (MeN_3, Me_2CO, *etc.*) is not far from that in the free ligand, as discussed below.

Nitrogen Co-ordination Shifts.—Nitrogen-15 shifts for the diamagnetic dinitrogen complex $[Ti(C_5Me_5)_2(N_2)]$, in toluene at −61 °C, have been interpreted [6] in terms of an equilibrium between two isomers, one with end-on co-ordination of dinitrogen, $>\mathrm{TiN{\equiv}N}$, giving two doublets (J 7 ± 2 Hz) with δ 499.6 and 549 p.p.m., the other with the dinitrogen edge-on, $>\mathrm{Ti}\!<\!\overset{\mathrm{N}}{\underset{\mathrm{N}}{|||}}$, giving a sharp singlet at δ 633.6 p.p.m. {The conversions into the $[NH_4]^+(aq)$ scale are given in the Appendix.} Such co-ordination shifts of 200—350 p.p.m. compared with the free ligand (N_2), CH_2N_2, and CH_2NN are much larger than those usually observed for nitrogen bonded to metals in diamagnetic complexes. For anionic ligands such as $[N_3]^-$,[12] NCO,[19a] and $[NCS]^-$,[19b] the metal-bonded nitrogen resonates a few tens of p.p.m. upfield of the free ligand, roughly in the region of nitrogen bonded to carbon in the methyl derivative (MeN_3, MeNCO, *etc.*). For the nitrile ligand,[19c] the co-ordination shift is again small and upfield (the nitrogen resonance is upfield of azomethine groupings $R_2C{=}NR$, though downfield of isocyanide and protonated nitrile). In nitrito-complexes and linear nitrosyls the bonded nitrogen resonance is in the region of $[NO]^+$, $[NO_2]^+$, and $[NO_3]^-$ (*i.e.* upfield of nitroso- and nitrito-compounds which have low-lying $n\rightarrow\pi^*$ states) and in the same region as $MeNO_2$. Similarly, ^{13}C resonances in carbonyl complexes are within 40 p.p.m. downfield of the free ligand, in the same region as the carbonyl carbon in aldehydes and ketones.[20,21]

Ligands bridging metal atoms don't usually show very large co-ordination shifts: carbon-13 in bridging carbonyl ligands in metal-cluster complexes resonates 50—60 p.p.m. downfield of singly attached CO,[22] but azide nitrogen bridging two palladium atoms in *N*-diazonium fashion, $\overset{\mathrm{M}}{\underset{\mathrm{M}}{}}\!>\!\mathrm{N{-}N{=}N}$, has the same chemical shift as nitrogen in singly attached azide, 45 p.p.m. upfield of MeN_3.[12]

The small co-ordination shifts can be explained by compensating σ-donor and π-acceptor effects in the complex, both n and π^* levels being stabilised when the ligand bonds to the metal.[20] For nitrogen non-bonded to the metal the co-ordination shift is usually smaller still and downfield (correlating with π^* stabilisation), *e.g.* for $[N_3]^-$,[12] $[CN]^-$,[20] RNC,[19c] $[CNO]^-$,[19d] $[SCN]^-$,[19b] *etc.*

The resonance for molecular nitrogen as we have seen is close to that in diazirine and midway between those in CH_2NN, at 265 and 369 p.p.m. Thus dinitrogen resonances in complexes, if they follow the pattern of the related ligands, are expected to be in the region of 300 ± 100 p.p.m. (in the absence of contact or pseudo-contact shifts). A small downfield shift may be found in π-electron-deficient titanium complexes. Comparison with Table 1 shows that the coupled dinitrogen resonances in the titanocene complex are in the alkylazo- and carboxylazo-region, and the third line is further downfield, in the nitroso-region.[7] Therefore either the co-ordination shifts in the titanocene complexes fall outside the general pattern described above, or perhaps the complexes, in this rather labile system, contain bridging nitrogen corresponding to an azo-group.

EXPERIMENTAL

Diazirine was made by the method of Schmitz and Ohme,[23] and diphenyldiazomethane by Eastlick's method.[24] Nitrogen-14 shifts were measured with a Varian 4300B spectrometer at 3 MHz using phase-sensitive detection of the centre band at 40 Hz modulation, or of the side band at

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[19] (*a*) K. F. Chew, W. Derbyshire, N. Logan, A. H. Norbury, and A. I. P. Sinha, *Chem. Comm.*, 1970, 1708; (*b*) O. W. Howarth, R. E. Richards, and L. M. Venanzi, *J. Chem. Soc.*, 1964, 3335; (*c*) W. Becker, W. Beck, and R. Rieck, *Z. Naturforsch.*, 1970, **B25**, 1332; (*d*) W. Becker and W. Beck, *Z. Naturforsch.*, 1970, **B25**, 101.

[20] R. Bramley, B. N. Figgis, and R. S. Nyholm, *J. Chem. Soc.* (*A*), 1967, 861.

[21] J. B. Stothers, 'Carbon-13 NMR Spectroscopy,' Academic Press, 1972, ch. 8.

[22] B. F. G. Johnson, Dalton Symposium, 12th February, 1974.

[23] E. Schmitz and R. Ohme, *Chem. Ber.*, 1962, **95**, 795.

[24] S. G. Kukolich and S. C. Wofsy, *J. Chem. Phys.*, 1970, **52**, 5477.

500 Hz, and saturated aqueous ammonium nitrate as external reference.

APPENDIX

The Absolute Scale of Nitrogen Shielding.—The values for the absolute shielding, σ, given in Table 3 were obtained by referring the chemical shift δ {relative to $[NH_4]^+$(aq), downfield positive} to an absolute scale based on the molecular-beam maser measurement [24] of the spin-rotation constants for ^{14}N in NH_3, $C_{\perp}^{N} = 6.77(2)$ and $C_{\parallel}^{N} = 6.71(2)$ kHz (the figure in parentheses gives the uncertainty in units of the last digit). With the equation for symmetrical-top molecules given by Flygare,[25] these give a value of -91 p.p.m. for the paramagnetic term σ_p in NH_3(g), vibrational effects being neglected. The diamagnetic term, σ_d, has been calculated (*ab initio*) [26] as 355 p.p.m., and these together give the absolute shielding for nitrogen in NH_3(g) as 264 p.p.m. The nitrogen shielding in $[NH_4]^+$(aq) can be related to that in NH_3(g) by ^{15}N measurements. Alei and his co-workers have given the chemical shifts of NH_3(g) and $[NH_4]^+$(aq) relative to NH_3(l) as -18 [27] and 26.1 p.p.m.[28] respectively, from which $[NH_4]^+$(aq) has σ(N) = 220 p.p.m. {Their measurements [28] were also used to express Bercaw's shifts relative to $[NH_4]^+$(aq).}

The absolute scale can be checked against the spin-rotation measurements on $H^{12}C^{14}N$ when the chemical shift has been measured: the constant $C^N = 10.4(3)$ kHz (measured by molecular-beam maser) [29] with Ramsey's equation for linear molecules [18] gives $\sigma_p^N = -411$ p.p.m., and this with $\sigma_d = 381$ p.p.m.[30] gives the absolute shielding of nitrogen in HCN(g) as -30 p.p.m. Our earlier scale [31] used older and less-precise spin-rotation measurements on $^{15}N_2$,[32a] coupled with a measurement [13] of the chemical shift of liquid nitrogen, for which a more accurate value is now available,[32b] and a calculated σ_d.[33]

In Table 3 the values of σ_d were calculated by Flygare and Goodisman's equation [34] and are likely to be accurate within a couple of p.p.m. This diamagnetic term is summed over all atoms in the molecule,[18] in contrast to the Slichter–Pople local term, σ_d^A, which takes account only of electrons on the atom (A) in question.[17] In our earlier studies [1,7,31] an atom-plus-ligand local term (which we can call σ_d^{AL}), summed over the atom in question and the immediate ligands L, was used as a diamagnetic correction of the observed shifts. This afforded a measure of σ_p^{AL} which gave better 'chemical' correlations, such as additivity of substituent effects, than the observed shifts do, both in nitrogen [31] and in carbon shielding.[35] In our present discussion the molecules are sufficiently small for all-atom shielding terms to be used. The $\langle r^{-3}\rangle_{2p}$ values in Table 3 are taken from shielding calculations [36] which follow the Pople theory [16] and use a modified CNDO–CI method [37] for molecular orbitals and energies. Slater's rules are extended to atoms with fractional electron populations to give the radial term, the relative values of which are acceptable for our present purpose.

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