Fig. 1.—Confirmation of tin atoms in $((C_6H_5)_2Sn)_6$.

X-ray study. A light yellow powder, obtained by adding methanol to an ether solution of diphenyltin dihydride, was dissolved in dimethylformamide. The resulting crystals were recrystallized in *m*-xylene. The well-formed, clear, colorless crystals which resulted are monoclinic with $a = 12.05$, $b = 18.17$, $c = 18.55$ Å., and $\gamma = 102.7°$. $P2_1/b$ is the probable space group. There are twelve diphenyltin units and four xylene molecules per unit cell; the calculated density is 1.55 g./cc. *vs.* 1.55 g./cc. observed. Complete three-dimensional data were collected on a G.E. XRD-5 crystal orienter using Mo $K\alpha$ irradiation. These data were corrected for background, streaking, absorption, and Lorentz-polarization factors. The three independent tin positions were obtained from a three-dimensional Patterson map and refined to a reliability index of 27% using 607 reflections with 2θ less than 25°. The positions of all carbon atoms were found from subsequent Fourier maps. The atomic parameters, including anisotropic thermal parameters, were refined using the block diagonal least squares method. The final R values for all data and for observed reflections only are 15.9 and 7.2%, respectively. Final analysis of this structure is still in progress. A full account of this X-ray work is to be published elsewhere.

Discussion

The three asymmetric tin atoms are related to three more by a center of symmetry forming a six-membered ring with the chair configuration. The tin–tin bonds (Fig. 1) have lengths of 2.77, 2.78, and 2.78 Å., compared with the tin–tin distance of 2.80 Å. in gray tin, indicating normal tetrahedral covalent bonds. Two phenyl groups emanate from each tin atom at approximately tetrahedral angles. The xylene molecule is not involved in any type of π-bonding with the tin atoms.

It is not to be expected that R_2Sn compounds will remain monomeric, since this would leave a valence orbital of tin vacant and is contrary to valence principles which have now been established.[11] It is interesting to note that for R_2Sn compounds, where R is an organic group, the tendency to use all valence orbitals leads to tin–tin bonds and to tetravalent tin. In inorganic compounds,[12] it is most usual to find that tin(II) uses its three 5p-orbitals to form three electron-pair

bonds either by forming halogen bridges or by accepting electron pairs from such donors as water.[12] Without tin–tin bonds in R_2Sn compounds, the extra valence orbital could only be filled by some sort of bond delocalization as, for example, in trimethylaluminum,[13] and in organometallic tin compounds it is apparently energetically more favorable to form electron-pair tin–tin bonds. In inorganic compounds, where unshared pairs abound, tin(II) is stabilized by acting as an electron acceptor for some of these unshared pairs to form nondelocalized electron pair bonds.

(13) P. H. Lewis and R. E. Rundle, *J. Chem. Phys.*, **21**, 986 (1953).

CONTRIBUTION FROM THE ROHM AND HAAS COMPANY,
REDSTONE ARSENAL RESEARCH DIVISION,
HUNTSVILLE, ALABAMA

Further Nuclear Magnetic Resonance and Electron Paramagnetic Resonance Studies on the System $N_2F_4 \rightleftharpoons 2NF_2$

BY RAYMOND ETTINGER AND CHARLES B. COLBURN

Since the first synthesis of tetrafluorohydrazine in 1958[1] and the observation of the dissociative equilibrium between tetrafluorohydrazine and the difluoramino free radical,[2,3] considerable interest has been shown in many of the physical properties of this system. We wish to report here some further observations on the n.m.r. and e.p.r. spectra of this system.

E.p.r. Spectrum

The first e.p.r. spectrum of NF_2 was observed in the gas phase at approximately 40 mm. pressure and over the temperature range 340–435°K.[4] The spectrum observed was a single broad line with a g-value of 2.010 and a peak to peak line width of 104 gauss. Recently, the spectrum of NF_2 in solid argon has been observed.[5] In the solid matrix, Adrian and co-workers were able to observe some hyperfine structure; in particular, a center triplet arising from interaction with the N^{14} nucleus (16 gauss) and corresponding to the NF_2 spin state in which the two fluorine nuclei are antiparallel. Two side lines were also found about 47 gauss from the center line, but, like the outer lines of the triplet, they

(11) (a) R. E. Rundle, *J. Am. Chem. Soc.*, **69**, 1327, 2075 (1947); (b) *J. Chem. Phys.*, **17**, 671 (1949).

(12) SnS: W. Hofmann, *Z. Krist.*, **92**, 161 (1935); SnSe: A. Okazaki and I. Ueda, *J. Phys. Soc. Japan*, **11**, 470 (1956); SnCl₂: J. M. Van den Berg, *Acta Cryst.*, **14**, 1002 (1961); SnCl₂·2H₂O: B. Kamenar and D. Grdenic, *J. Chem. Soc.*, 3954 (1961); K₂SnCl₄·H₂O: B. Kamenar and D. Grdenic, *J. Inorg. Nucl. Chem.*, **24**, 1039 (1962); SnSO₄: P. J. Rentzeperis, *Z. Krist.*, **117**, 431 (1962). See also R. E. Rundle and D. H. Olson, *Inorg. Chem.*, submitted for publication.

(1) C. B. Colburn and A. Kennedy, *J. Am. Chem. Soc.*, **80**, 5004 (1958).

(2) C. B. Colburn and F. A. Johnson, *J. Chem. Phys.*, **33**, 1869 (1960).

(3) F. A. Johnson and C. B. Colburn, *J. Am. Chem. Soc.*, **83**, 3043 (1961).

(4) L. H. Piette, F. A. Johnson, K. A. Booman, and C. B. Colburn, *J. Chem. Phys.*, **35**, 1481 (1961).

(5) F. J. Adrian, E. L. Cochran, and V. A. Bowers, "Free Radicals in Inorganic Chemistry," Advances in Chemistry Series, No. 36, American Chemical Society, Washington. D. C. 1962. p. 50.
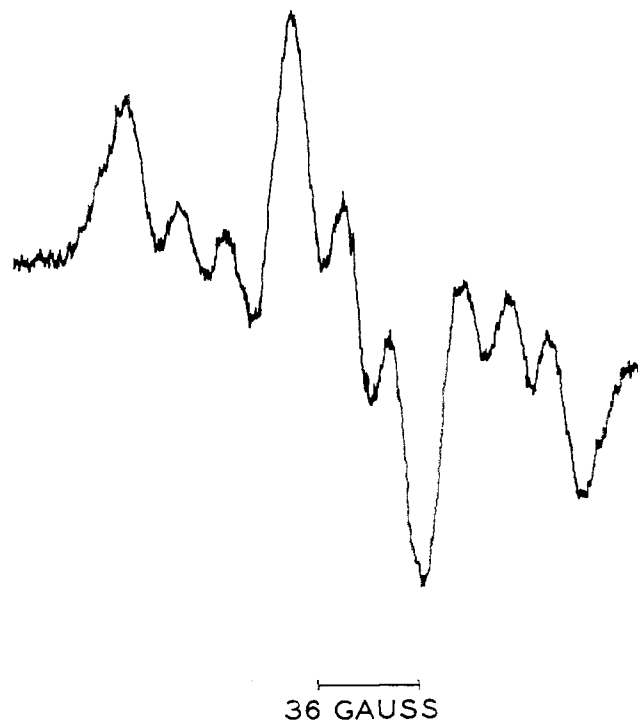
36 GAUSS

Fig. 1.—E.p.r. spectrum of NF_2 in perfluorodimethylhexane.

Fig. 2.—The F^{19} n.m.r. spectrum of N_2F_4 (cycles per second downfield from trifluoroacetic acid).

were weak, broad, and unsymmetrical. Apparently the N^{14} structure was washed out in these side lines. The weak and broadened features of Adrian's spectrum were due to the anisotropic nature of the interactions at low temperature and the spectrum was not greatly improved when the matrix sample was warmed. Even more recently, Doorenbos and Loy[6] have reported a broad e.p.r. signal in the vapor phase at 25° and 13 atm. pressure. In the liquid phase they found a triplet believed to arise from the two equivalent fluorine atoms, the nitrogen splitting apparently remaining unresolved. They reported a g-value of 2.006.

Figure 1 depicts a first derivative spectrum of NF_2 which has been almost completely resolved into nine components. This spectrum was obtained at room temperature, with tetrafluorohydrazine dissolved in perfluoro-2,3-dimethylhexane. Similar spectra have also been observed when N_2F_4 was dissolved in Kel F[7] oils No. 1, 3, and 10 and in 2,2-dichloro-3-chloroperfluorobutane.

The following observations have been made on this spectrum. There are nine overlapping lines which are interpreted as consisting of a 1:2:1 triplet, each component being split further into a 1:1:1 triplet. The measured N^{14} and F^{19} couplings are 16 and 56 gauss, respectively, and the over-all peak-to-peak width was approximately 150 gauss. The g-value was determined to be 2.009.

We believe the failure of earlier investigators to obtain complete resolution of this spectrum may be due (at least in part) to the presence of the paramagnetic impurity NO in their N_2F_4. It is a very common im-

purity in N_2F_4 and we have found that as little as 1% NO can cause poor resolution of the NF_2 e.p.r. signal.

Discussion

The unpaired electron in a bent triatomic molecule with 19 valence electrons (NF_2, NO_2^{-2}, O_3^-, SO_2^-, ClO_2, etc.) should lie in a relatively pure π level and there should be small s character with respect to the central atom. Results for NF_2 were in accord with this picture, and the general trend discussed by Symons and co-workers.[8-11] The average g-values reported for NF_2 and other radicals with 19 valence electrons lie in the range 2.005–2.010, considerably above the free electron value.

The unpaired electron in NF_2 is predicted[12] to be in a $2b_1$ molecular orbital constructed by out-of-phase overlap of the three px-orbitals perpendicular to the molecular plane (which contains the Y and the Z axes, the latter bisecting the FNF angle). Thus

$$\Psi(NF_2) = a_{px}\Psi_N(2px) - b_{px}(1/\sqrt{2})[\Psi_F(2px) + \Psi_{F'}(2px)]$$

$$a_{px}^2 + b_{px}^2 = 1$$

The greatest hyperfine coupling should occur for the field in the X-direction assuming a positive isotropic coupling constant. The unpaired electron presumably polarizes the $4a_1$ molecular orbital which has 2pz and 2s character on nitrogen, accounting for the small

(6) H. Doorenbos and B. R. Loy, *J. Chem. Phys.*, in press.
(7) Trade Mark of the Minnesota Mining & Manufacturing Company, St. Paul, Minn.

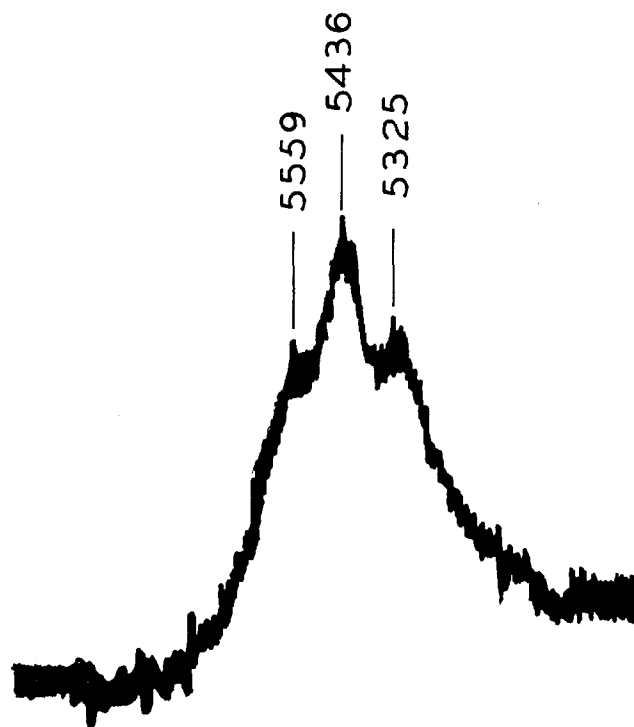(8) M. C. R. Symons, ref. 5, p. 76.
(9) P. W. Atkins, N. Keen, and M. C. R. Symons, *J. Chem. Soc.*, 2873 (1962).
(10) P. W. Atkins, J. A. Brivati, N. Keen, M. C. R. Symons, and P. A. Trevalion, *ibid.*, 4785 (1962).
(11) P. W. Atkins and M. C. R. Symons, *ibid.*, 4794 (1962).
(12) A. D. Walsh, *ibid.*, 2266 (1953).

isotropic coupling, 16 gauss, observed in the spectrum in Fig. 1. This value is close to those found in several radicals[8] having similar electronic configuration. The isotropic interaction is related to the spin population, $a_s{}^2$, of a nitrogen s-orbital by the expression

$$A_{iso} = g_N\beta_N(8\pi/3)|\Psi_{2s}(0)|^2 a_s{}^2$$

where g_N and β_N are the nuclear g-value and magneton, respectively, and $\Psi_{2s}(0)$ is the amplitude of the wave function of the 2s-orbital at the nucleus. Employing[13,14] $|\Psi_{2s}(0)|^2 = 34.0 \times 10^{24}$ cm.$^{-3}$, it is calculated that $a_s{}^2 = 0.028$ in NF_2. Atkins and Symons[11] found 0.027 for the corresponding quantity in $NO_2{}^{-2}$. (The rough nature of such quantitative estimates of relative s and p character has been discussed by Symons.[8])

Assuming that the isotropic fluorine interaction arises from the exchange polarization of a fluorine 2s-orbital, then the preceding expression may be adapted to find $b_s{}^2$. The self-consistent field functions for F^- calculated by Löwdin[13] and Allen[15] give an electron density $|\Psi_{2s}(0)|^2 = 11.0$ a.u. at the fluorine nucleus. For an F atom, the density would be 11.5 a.u. Taking the density to lie within the latter range, the calculated fluorine 2s character ($b_s{}^2$) is 0.003; the result is small as anticipated.

As in Symon's treatment, $a_{pz}{}^2$ may be estimated from Coulson's[16] hybridization relationships and the requirement that the nitrogen's contribution to the $4a_1$ orbital be orthogonal to the NF bond-forming orbitals. From the valence angle,[17] 104°, in NF_2 and the relation

$$\alpha = 2\cos^{-1}(\lambda^2 + 2)^{-1/2} \text{ where } \lambda = a_{pz}/a_s$$

the value for $a_{pz}{}^2$ is calculated to be 0.018.

(13) P. O. Löwdin, *Phys. Rev.*, **90**, 120 (1953).
(14) G. C. Dousmanis, *ibid.*, **97**, 967 (1955).
(15) L. C. Allen, *J. Chem. Phys.*, **34**, 1156 (1961).
(16) C. A. Coulson, "Victor Henri Memorial Volume," Desoer, Liége, 1948, p. 15.
(17) M. D. Harmony, R. J. Myers, L. J. Schoen, D. R. Lide, and D. E. Mann, *J. Chem. Phys.*, **35**, 1129 (1961).

The distribution of unpaired electron spin in the px orbitals (perpendicular to the molecular plane) cannot be determined without experimental knowledge of the anisotropic hyperfine interaction tensor. However, spectra thus far obtained[5] from NF_2 radicals randomly trapped have not been sufficiently informative. By analogy with $NO_2{}^{-2}$, $a_{px}{}^2$ would be expected to be of the order of 0.50 or greater.

N.m.r. Spectrum

The coupling of the equivalent fluorine nuclei to the nitrogen nuclei in N_2F_4 would be expected to give rise to a triplet in the F^{19} spectrum. However, as in the case of NF_3,[18] at low temperature, the triplet in N_2F_4 has not previously been observed due to quadrupole relaxation. However, when N_2F_4 is dissolved in perfluoro-2,3-dimethylhexane at room temperature, a triplet n.m.r. is observed as illustrated in Fig. 2. The N^{14}–F^{19} coupling constant is ~117 c.p.s., which may be compared[19] with J_{N-F} in the difluorodiazine isomers (145 c.p.s. *cis*, 136 c.p.s. *trans*) and in NF_3 (155 c.p.s.).

Experimental

(18) E. L. Muetterties and W. D. Phillips, *J. Am. Chem. Soc.*, **81**, 1084 (1959).
(19) J. H. Noggle, J. D. Baldeschwieler, and C. B. Colburn, *J. Chem. Phys.*, **37**, 182 (1962).

Correspondence

The Structure of Triiron Dodecacarbonyl

Sir:

The recent paper by Herber and co-workers[1] which presented evidence for a "staggered" 3-3-3-3[2] structure for triiron dodecacarbonyl ($Fe_3(CO)_{12}$) and for the presence of carbonyl bridges in this complex prompts us to report evidence which also supports this view.

Much of the data which have been reported in regard to the existence of ketone-like carbonyl bridges have been reviewed in Herber's paper. Barraclough and co-workers,[3] however, have reported solvent shift studies

(1) R. H. Herber, W. R. Kingston, and G. K. Wertheim, *Inorg. Chem.*, **2**, 153 (1963).
(2) F. A. Cotton, A. D. Liehr, and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **2**, 141 (1956).
(3) C. C. Barraclough, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 2582 (1961).

in which significant downward shifts in the bridging frequencies for $Co_2(CO)_8$ are observed in more polar solvents, while no such trend is evident for the terminal carbonyl groups of this complex or for $Fe(CO)_5$. That work also pointed out the similarity between the shifts observed for the bridging carbonyl bands in $Co_2(CO)_8$ and those reported[4] for various ketones.

We have extended the solvent shift studies to $Fe_3(CO)_{12}$ and find that the stronger of the two bands in the bridging carbonyl region shifts in much the same manner as do the bridging carbonyl bands in $Co_2(CO)_8$ and in ketones; no studies were made on the other band because of its weak intensity. Table I gives the results for this work which is, we believe, still further evidence for the presence of bridging carbonyl bands in

(4) L. J. Bellamy and R. L. Williams, *Trans. Faraday Soc.*, **55**, 14 (1959).