Scheme I. Preparation of Triamines

1a, $n = 2$
b, $n = 3$

2a, $n = 5$
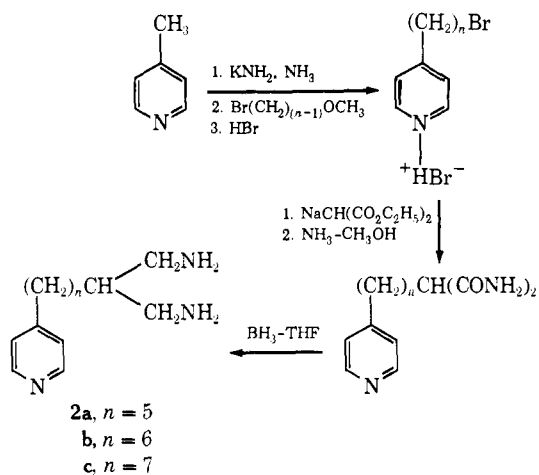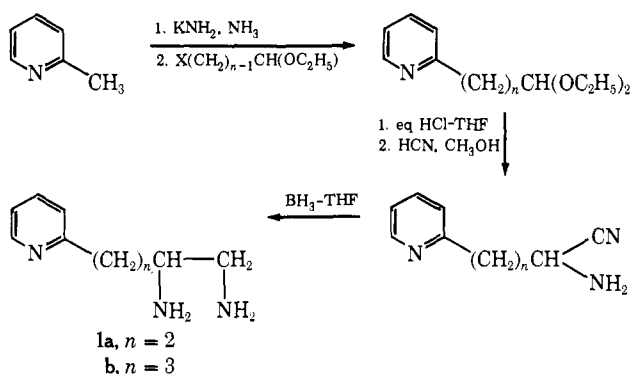b, $n = 6$
c, $n = 7$

Figure 1. Perspective view of one molecule of $CoC_{25}N_3O_2H_{21}$.

amidal arrangement of nitrogen and oxygen donors about their central cobalt atoms (Figure 1). The basal plane of this bipyramid contains the atoms N(1), O(2), N(3), and Co. One consequence of this ligation is a pronounced twist (dihedral angle 24°) between the six-membered salicylaldehyde rings which include the cobalt atom. Another is a statistically significant difference between Co–N bond lengths which average 2.15 Å for the pyridyl group and 1.96 Å otherwise.

Each molecule is hydrogen bonded to a separate ethanol solvate molecule. The hydrogen bond lengths O(1)–O(3) in both situations are 2.82 Å where O(3) is the oxygen atom in an ethanol molecule. Our calculations and packing diagrams absolutely exclude the possibility of any intermolecular coordination in a sixth position on either cobalt atom.

This five-coordinate Co(II) molecule assumes special interest because its mononuclear dioxygen adduct has been prepared, characterized, and crystallized in the monoclinic space group $P2_1/c$ with four molecules in a unit cell of dimensions $a = 9.566(1)$, $b = 19.466(3)$, $c = 12.773(2)$ Å, and $\beta = 106.03(1)°$. Structure analysis is severely hindered by the presence of disordered solvate molecules but preliminary results ($R = 0.10$) confirm the bent mode of bonding found for one other dioxygen adduct of cobalt[6] and, also, demonstrate significant stereochemical rearrangement of the five-coordinate complex so that the Schiff base adopts a nearly planar arrangement in the six-coordinate product molecule.

Other pentacoordinate ligand systems, and their transition metal complexes, have been prepared from

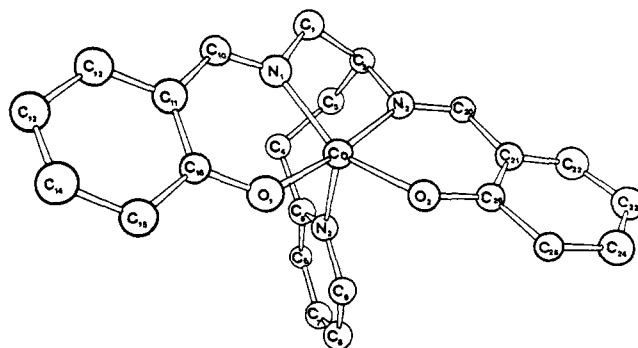(6) G. A. Rodley and W. T. Robinson, *Nature (London)*, **235**, 438 (1972).

these substituted en and pn derivatives and will be described subsequently.

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The α,α-Difluorobenzyl Radical and Its Analogs. The Question of Planarity[1]

Sir:

The difluorobenzyl cation, $PhCF_2^+$, was shown to be planar by both the ^{13}C and ^{19}F nmr studies of Olah, *et al.*[2,3] Strong back π-bonding from F to C exists in this cation. Conversely, the difluorobenzyl anion, $PhCF_2^-$, is known to be tetrahedral.[4,5] Apparently, this is due to repulsive interactions between the fluorine lone pairs and the π electrons of the sp^2-hybridized carbon of the planar anion.[5,6] What, then, is the geometry of the difluorobenzyl radical, $Ph\dot{C}F_2$ (1)? It is well known experimentally and theoretically that radicals $R\dot{C}F_2$ have a tendency to be nonplanar.[7–9] Could the phenyl group provide enough conjugative stabilization to overcome the tendency of $R\dot{C}F_2$ to be nonplanar? We now present esr and theoretical evidence which indicates radical 1 is planar with a shallow out-of-plane energy well.

Radical 1 and its *p*-fluoro analog 2 were obtained

(1) This research was partially supported by the U. S. Atomic Energy Commission, Contract No. AT-(40-1)-4062, and partially by The University of Alabama Research Grants Committee under Grant No. 600 and 672. This is AEC Document ORO-4062-9. The University of Alabama Computer Center generously provided computer time.

(2) G. A. Olah and M. B. Comisarow, *J. Amer. Chem. Soc.*, **91**, 2955 (1969).

(3) G. A. Olah, Y. K. Mo, and Y. Halpern, *ibid.*, **94**, 3551 (1972).

(4) For a detailed discussion, see D. Holtz, *Progr. Phys. Org. Chem.*, **8**, 1 (1971).

(5) A. Streitwieser, Jr., and F. Mares, *J. Amer. Chem. Soc.*, **90**, 2444 (1968).

(6) K. J. Klabunde and D. J. Burton, *ibid.*, **94**, 820, 5985 (1972).

(7) For example, $\cdot CF_2H$ and $\cdot CF_3$ are nonplanar (R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **43**, 2704 (1965)), while $^+CF_2H$ and $^+CF_3$ are planar (L. D. Kispert, C. U. Pittman, Jr., D. L. Allison, and T. B. Patterson, *J. Amer. Chem. Soc.*, **94**, 5979 (1972)).

(8) D. M. Schrader and M. Karplus, *J. Chem. Phys.*, **40**, 1593 (1964); K. Morokuma, L. Pedersen, and M. Karplus, *ibid.*, **48**, 4802 (1968).

(9) D. L. Beveridge, P. A. Dobosh, and J. A. Pople, *ibid.*, **48**, 4802 (1968).

Table I. Observed Coupling Constants (Gauss)

Radical	Solvent[a]	Temp, °C	a_{H_m}[e]	a_{H_o}[e]	a_{H_p}[e]	a_{F_p}	$a_F{}^{CF_2}$
1	70% CP, 20% P, 10% DTP	−60	1.6_1	4.7_5	5.6_4		Not obsd
1	70% CCl₄, 20% P, 10% DTP	+30	1.6_1	4.7_5	5.6_5		51.4 ± 0.2
2	50% P, 50% DTP	+48	1.6_0	4.84		12.50[b]	56.3 ± 0.2
3[e]	70% CCl₄, 20% P, 10% DTP	−32	1.6^e	4.8^e	$a_H{}^{CF_2H}$ 2.2[e]	$a_F{}^{CF_2H}$ (18.0)[c,d]	$a_H{}^{CH_2}$ 16.8
Benzyl[10a]	30% toluene in ethane	−93	1.7_7	5.1_5	6.1_8		$a_H{}^{CH_2}$ 16.30

[a] P stands for the radical precursor, DTP for di-tert-butyl peroxide, and CP for cyclopropane. [b] In 67% CP, 11% DTP, and 22% P at −65°, a_{F_p} = 12.82 G but no $a_F{}^{CF_2}$ was observed. [c] Computer simulation best fit values. [d] Estimated value, weak signals prevented the observation of all of the outer wings necessary for measurement of this splitting. In fact, values of 14.0 G gave better fits to the center of the spectra. [e] Average of several measurements, deviation ±0.03 G.
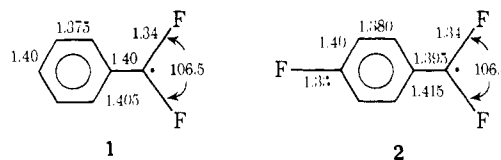
during steady-state photolysis of α,α-difluorotoluene (or its p-fluoro analog) and di-tert-butyl peroxide.[10,11] The precursors, p-XPhCF₂H, were prepared by the reaction of SF₄ with the appropriate benzaldehyde.[12] The outer fluorine lines of 1 (high and low field) were very broad,[13] a result of the rotational modulation of the ¹⁹F anisotropic hyperfine interactions.[13,14] The outer lines could only be seen in solvents of low viscosity at elevated temperatures (40–50°) using microwave power levels ten times that normally used in photolysis studies where line widths are 0.05–0.1 G.[15] Similar results were obtained for 2. The photolysis of p-chloro-α,α-difluorotoluene gave only a very weak three-line 1:2:1 triplet with a 1-G splitting. This disappeared after about 10 min during photolysis. Photolysis of p-methyl-α,α-difluorotoluene leads primarily to ·CH₂C₆H₄CF₂H (3). The esr data are summarized in Table I.

The most notable features of the spectra of radicals 1 and 2 are the small α-fluorine hyperfine splittings (51.4 and 56.3 G, respectively). These values compare closely to the experimental isotropic coupling of 56.4 G observed for ·CFHCONH₂,[16] a radical which was calculated, by optimized INDO methods, to be planar with $a_F{}^{CFH}$ = 58.9 G.[17] This suggests 1 and 2 are planar. Analogous esr studies of nonplanar radicals include ·CF₂CONH₂ ($a_F{}^{CF_2}$ = 72 G),[18] ·CF₂H (84.2

G),[7] and ·CF₂COO⁻ both in solution (64 G)[13] and in a single crystal (72.4 G).[19] This series emphasizes that the isotropic fluorine coupling increases as the geometry becomes nonplanar.[7,9]

Furthermore, a^F is 50.1 G in ·CFClCONH₂ for which a planar configuration was calculated.[17] Thus, the low a^F value of 1 compared to that for ·CF₂CONH₂ (68–72 G) could logically arise from a planar CF₂ group resulting in a small unpaired 2s orbital fluorine spin density. However, a significant withdrawal of spin density by the aromatic ring might also lower the a^F value.[20]

Thus, INDO–LCAO–SCF calculations were carried out on radicals 1 and 2 in the INDO approximation.[21] First, a symmetrical phenyl ring was assumed (C–C bonds set at 1.39 Å), and the bonds about the carbinyl carbon were optimized (C–F = 1.34 and C–C = 1.40 Å). The most stable conformation for this geometry was all-planar for both 1 and 2. Optimization of the ring bond lengths was then carried out. For both 1 and 2 the most stable geometries had the quinoid structures summarized below. Again, the all-planar

conformations of the quinoid structures were the most stable. Deforming the CF₂ group out of the plane resulted in an increase in energy, but the potential wells were very shallow for a series of α,α-difluorobenzyl radicals.[22]

Some unpaired spin density in 1 has been withdrawn from the benzylic carbon's 2p π orbital and to a lesser degree from the $C_{2s}{}^\alpha$ and $F_{2s}{}^\alpha$ orbitals.[20] The fluorine 2s unpaired spin density increases by the same amount

(10) This method was pioneered by (a) P. J. Krusic and J. K. Kochi, J. Amer. Chem. Soc., 90, 7155, 7157 (1968); (b) ibid., 91, 1877, 1879, 3938, 3940, 3942, 3944, 6161 (1969), 93, 846 (1971).

(11) The esr measurements were carried out on a Varian E-12 esr spectrometer coupled to a Varian SS-100 computer. All spectra were calibrated using a tracking nmr system. Simulations of spectra were performed on the Varian SS-100. The uv photolysis system used in this study was previously described; see L. D. Kispert, R. C. Quijano, and C. U. Pittman, Jr., J. Org. Chem., 36, 3837 (1971).

(12) W. R. Hasek, W. C. Smith, and V. A. Engelhardt, J. Amer. Chem. Soc., 82, 543 (1960).

(13) Broad outer ¹⁹F lines were reported for the ·CF₂COO⁻ radical during the course of this work: J. Cooper, A. Hudson, R. A. Jackson, and M. Townson, Mol. Phys., 23, 1155 (1972).

(14) Personal communication, P. J. Krusic.

(15) Only the central $m_I{}^F$ = 0 line of the –CF₂ group was observed at −60° in cyclopropane. However, photolysis of a 50:50 mixture of α,α-difluorotoluene and di-tert-butyl peroxide or a solution consisting of 10% peroxide and 20% precursor in CCl₄ led to the observation of the high- and low-field ($m_I{}^F$ = ±1) lines.

(16) R. J. Cook, J. R. Rowlands, and D. H. Whiffin, Mol. Phys., 7, 31 (1964).

(17) L. D. Kispert and F. Myers, Jr., J. Chem. Phys., 56, 2623 (1972). Calculations indicated the CFH plane made an angle of 0.5° with the plane of the amide group.

(18) M. T. Rogers and L. D. Kispert, ibid., 46, 3193 (1967); C. M. Bogan and L. D. Kispert, ibid., 57, 3109 (1972). Single-crystal splittings demonstrated the nonplanarity of ·CF₂CONH₂, and the CF₂ group was calculated to be 8° out of the plane of the amide group. The observed directions of the fluorine p orbitals in these single-crystal

studies confirmed the nonplanarity of ·CF₂CONH₂. This resulted in an umbrella-like inversion motion at low temperatures which was not observed (and cannot reasonably occur) for planar ·CFHCONH₂.

(19) M. T. Rogers and L. D. Kispert, ibid., 55, 2360 (1971).

(20) H. Fischer (Z. Naturforsch. A, 20, 428 (1965)) assigned the fraction of spin removal as 0.162 for COR and 0.072 for CO₂R. A similar amount is expected for CONH₂. We find the fraction removed by Ph is 0.236 while 0.148 was removed by CONH₂, according to geometry optimized INDO calculations. The value of ρ for the p orbital on carbon in 1 is 0.65 vs. 0.72 on planar ·CF₂CONH₂.

(21) D. L. Beveridge, P. A. Dobosh, and J. A. Pople, J. Chem. Phys., 48, 4802 (1968). QCPE Program No. 141 was used.

(22) The increase in energy for a 5° out-of-plane bend of the RCF₂ group was 0.1 kcal mol⁻¹ or less for radicals 1, 2, p-NO₂C₆H₄CF₂, and p-CF₃C₆H₄CF₂.

as the CF_2 group, of both 1 and $\cdot CF_2CONH_2$, is bent $10°$ out-of-plane ($\Delta = 0.0002$). Thus, the a^F values will increase as the geometry becomes tetrahedral. Based on $a^F = 51.4$ for planar 1, an isotropic $a^F = 62.6$ G is calculated for a $10°$ out-of-plane bend by INDO.[23] This calculated value (62.6) for nonplanar 1 can be compared to the experimentally observed a^F of 72 G for nonplanar $\cdot CF_2CONH_2$ where less withdrawal of spin density takes place.[18,20] This difference reflects the greater withdrawal of spin density by phenyl. Thus, the a^F (51.4) observed for 1 is still consistent with the planar geometry calculated by INDO.

The magnitude of all the $a^{F,H,\text{ or }13C}$ values varied only slightly, going from the symmetrical to the quinoid geometries in 1 and 2.[24] Progressively rotating the CF_2 plane out of the phenyl ring's plane in 1 and 2 resulted in moderate increases in the calculated $a_F^{CF_2}$ and $a_{13C}^{CF_2}$ splittings while the $a_{H_{o,m,p}}$ and a_{F_p} splittings decrease.[25] An 18 kcal/mol^{-1} barrier to this rotation is predicted in 1.

In summary, the experimental and theoretical results support all-planar geometries for 1 and 2.

(23) An unequivocal experimental or calculated value of isotropic fluorine splittings for planar 1, which explicitly defines the effect of spin density withdrawal on a^F, is desired. The discrepancy between the experimental and calculated hyperfine couplings for 1 and 2 was similar to that found previously for the benzyl radical, and ring geometry optimization improved the agreement; i.e., see J. A. Pople, D. L. Beveridge, and P. A. Dobosh, J. Amer. Chem. Soc., 90, 4021 (1968). The effects of new sets of spin coupling parameters, Q, in ab initio calculations of a_F as a function of geometry have been discussed (see H. Konishi and K. Morokuma, ibid., 94, 5603 (1972)), and the failure of expressions such as $a^F = Q_{eff} \, \rho\pi$ to predict experimental a^F values, even in a structurally related series of radicals, has been discussed (see M. Iwasaki, S. Noda, and K. Toriyama, Mol. Phys., 18, 201 (1970), and references therein).

(24) Very small absolute increases occurred for the values of $a_{H_{o,m,p}}$ while small decreases were observed for $a_F^{CF_2}$ and $a_C^{CF_2}$. These results are similar in magnitude and direction to those recently observed when the geometry of the benzyl radical was optimized; see D. L. Beveridge and E. Guth, J. Chem. Phys., 55, 458 (1971).

(25) The changes in the calculated hyperfine splittings going from the planar-quinoid geometry of 1 to that where the CF_2 plane is rotated $90°$ out-of-plane (and with a symmetrical ring) were a_{H_p} -5.61 to -0.16, a_{H_m} 3.29 to 2.08, a_{H_o} -5.83 to -1.75, $a_F^{CF_2}$ 39.9 to 44.4, and $a_{13C}^{CF_2}$ 29.9 to 35.0. These results are entirely consistent with similar calculations on the benzyl radical; see J. A. Pople and D. L. Beveridge, J. Chem. Phys., 49, 4725 (1968).

(26) Undergraduate summer research participant, 1972.

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Nuclear Magnetic Resonance Shift Reagents. The Question of the Orientation of the Magnetic Axis in Lanthanide–Substrate Complexes[1]

Sir:

The utility of nmr shift reagents which function predominantly by the dipolar mechanism for structural and stereochemical problems is becoming abundantly clear.[2] After a brief flurry of reports[2a] which indicated that the magnitude of the shifts induced by lanthanide

(1) Supported by the National Science Foundation and the Public Health Service, Research Grant No. GM-11072 from the Division of General Medical Sciences.

(2) (a) Cf. W. D. Horrocks, Jr., J. P. Sipe, III, and J. R. Luber, J. Amer. Chem. Soc., 93, 5258 (1971), and W. D. Horrocks, Jr., and J. P. Sipe, III, ibid., 93, 6800 (1971), for extensive references to earlier studies; (b) M. R. Willcott, III, R. E. Lenkinski, and R. E. Davis, ibid., 94, 1742 (1972), and R. E. Davis and M. R. Willcott, III, ibid., 94, 1744 (1972).
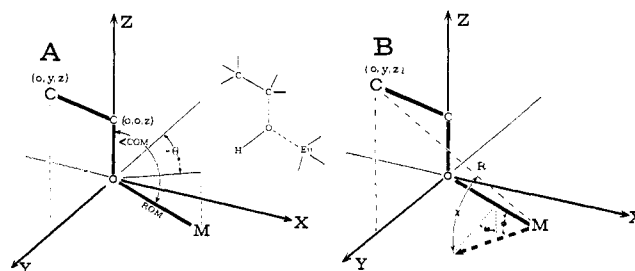
Figure 1. (A) Conventions for geometric parameters of metal atom in lanthanide chelate–alcohol complexes. (B) Parameters locating the principal magnetic axis with respect to the O–M bond. The angle ω is a dihedral angle for locating the magnetic dipole with respect to the O–C bond. It is defined as zero when the dipole lies in the plane determined by C–O–M and is on the opposite side of O–M from O–C.

chelates could be satisfactorily correlated by distance factors alone, the importance of angular factors, as predicted by the expected proportionality of the shifts to $(3 \cos^2 \chi - 1)/r^3$, which would lead to either upfield or downfield shifts with the same reagent–substrate complex, has been clearly established.[2] The $(3 \cos^2 \chi - 1)/r^3$ dependence, where χ is the angle between the principal magnetic axis of the complex and the vector of length, r, connecting the metal atom and nucleus under consideration, is justified strictly only for axially symmetric, or effectively axially symmetric, complexes. Nonetheless, excellent fits have been obtained following $(3 \cos^2 \chi - 1)/r^3$ proportionality with complexes of shift reagents and alcohols which can hardly be expected to be strictly axially symmetric and, furthermore, with the assumption that χ is, in fact, the angle between the vector r and the O–metal bond of the complex.[2b,3]

This assumption might well be justified on the basis that it works, but it seems imperative to know the limits which should be placed on it. To this end, we have undertaken the correlation of lanthanide-induced shifts of rigid alcohols without assuming that the O–M bond of the complex is necessarily collinear with the magnetic axis. The metal atom is defined in space with respect to the oxygen, C-1, and C-2 of the alcohol by the distance ROM and the angles $\angle$COM and θ (Figure 1A), while the orientation of the effective magnetic axis is defined by the angles ϕ and ω (Figure 1B). A computer program (CHMSHIFT) was used to find the best fit between observed lanthanide shifts and the five geometric and magnetic parameters for the metal atoms. The procedure involved maximizing the correlation coefficient for a least-squares fit of experimental[4] and calculated values of the shifts of both protons and ^{13}C resonances induced by praseodymium and europium chelates. No restrictions were placed on the values of

(3) (a) J. Briggs, F. A. Hart, and G. P. Moss, Chem. Commun., 1506 (1970); (b) J. Briggs, G. H. Frost, F. A. Hart, G. P. Moss, and M. L. Staniforth, ibid., 749 (1970); (c) J. Briggs, F. A. Hart, G. P. Moss, and E. W. Randall, ibid., 364 (1971); (d) the problem of the location of the principal magnetic axis has been considered very recently in a theoretical way by C. L. Honeybourne, Tetrahedron Lett., 1095 (1972). See also the papers of H. Huber, ibid., 3559 (1972); J. M. Briggs, G. P. Moss, E. W. Randell, and K. D. Sales, J. Chem. Soc., Chem. Commun., 1180 (1972).

(4) The experimental shifts were determined on 1 M solutions of substrate in deuteriochloroform with five or six concentrations of lanthanide chelate. The shifts were strictly linear with concentration (correlation coefficient >0.99). The shifts reported here in parts per million are extrapolated from the least-squares fit and represent hypothetical shifts at 1 M chelate concentration.