'Through-space' C_{sp}-F spin–spin couplings in fluoroarenes

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Dicyanomethylene fluoroarenes, in which interaction between non-bonding electrons of fluorine atom and one of CN groups is expected, have been prepared and their ^{1}H and ^{13}C{H} NMR spectra have been measured and interpreted in terms of 'through-space' ^{19}F,^{13}C coupling.

Keywords: spin–spin coupling, fluoroarenes

Spin–spin coupling depends on such factors as number of bonds separating coupled nuclei, their geometrical relation or electron properties of the substituents attached to the coupled system. For this reason, the measurements of spin–spin coupling constants are very useful in the investigation of the structure and stereochemistry of organic molecules. Usually, the information about spin states is transmitted with the aid of the bond electrons. In some sterically crowded molecules, however, this transmission may be realised predominantly by through-space interaction of nonbonding orbitals. Because in this case the coupling constant value is closely related to the spatial distance between nuclei it may sometimes be used as an important tool in solving stereochemical problems. It is known that the coupling of this type is especially effective when a fluorine nucleus is involved in the interaction. Several examples of F–F, F–H and F–C couplings have been reported in literature.[1–8] Continuing our study on "through-space" $^{13}C_{sp}$-^{19}F spin–spin coupling in chromium carbonyl complexes[9–11] we have paid our attention to the cyano group which is isoelectronic with the carbonyl one. We expected that the data obtained for cyano compounds might reveal some information concerning the relationship between C_{sp}–F coupling constant value and, firstly, the C–F distance and, secondly, the C–F and CN bonds orientation. As objects of our investigations, the following compounds were chosen: 9-dicyanomethylene-1-fluorofluorene, **1**, 10-dicyanomethylene-4-fluoro-1-methylanthrone, **2**, and 4-fluoro-5-dicyanomethylene-5*H*-dibenzo[a,d]cycloheptene, **3**.

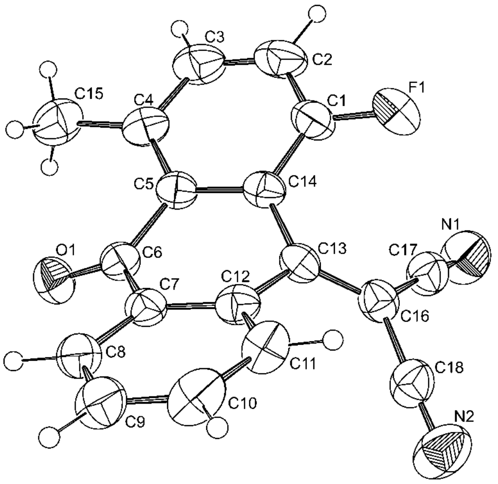
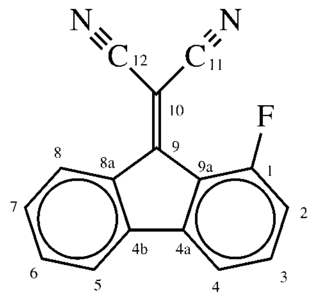


Fig. 1 ORTEP[29] plot of the molecular structure of **2** with thermal ellipsoids drawn at 50% probability level. Selected bond lengths (Å) and angles (°): F(1)–C(1) 1.354(2), O(1)–C(6) 1.2187(19), N(1)–C(17) 1.135(2), N(2)–C(18) 1.137(2), N(1)–C(17)–C(16) 176.4(2), N(2)–C(18)–C(16) 176.16(18), C(17)–C(16)–C(18) 112.75(14). Selected torsion angles (°): C(16)–C(13)–C(14)–C(1) –46.0(2), C(16)–C(13)–C(12)–C(11) 41.7(2), O(1)–C(6)–C(5)–C(4) 22.8(2), O(1)–C(6)–C(7)–C(8) –19.4(2).



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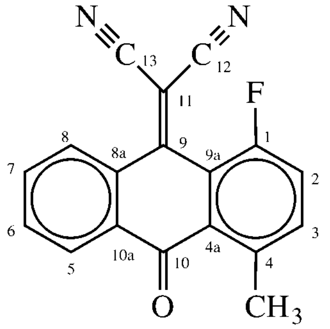

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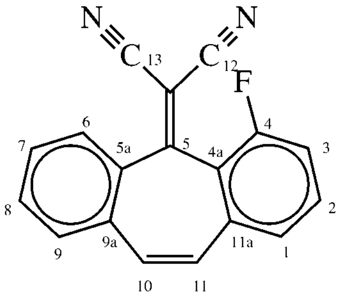

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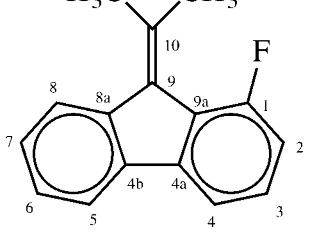

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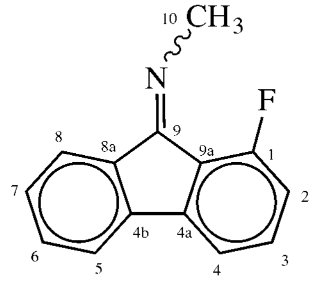

5E, 5Z

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Three other compounds, 1-fluoro-9-isopropylidenefluorene, **4** and isomers *E* and *Z* of *N*-(1-fluorofluoren-9-ylidene) methylamine, **5*E*** and **5*Z***, in which C–H bond orbital can take part in the transmission of information about the spin states between fluorine and methyl carbon atoms, have also been included for comparison.

Results and discussion

The most detailed investigation has been performed for compound **2**. Its solid state structure has been established by X-ray crystallography (see below). The central ring of this compound has been found not to be planar but to have a boat-like conformation. Inspecting the ^{13}C NMR data of **2** (experimental) one may find that only two of five, five-bond C,F couplings are sizable enough to give visible splittings in the spectrum. This applies to carbon atoms of both cyano groups. The problem of assigning the appropriate ^{13}C signals to cyano groups occupying particular stereochemical positions was solved on the basis of the result of heteronuclear Overhauser effect measurement. The NOE enhancement factors, due to saturation of proton signals, were found to be 2.97 for protonated carbon atoms and 1.17 and 1.02 for C13 and C12, respectively. Moreover, η values as well as longitudinal relaxation times, $T_{1,}$ for all protonated carbon atoms are very similar. It means that the higher value of ^{5}J(C,F), 2.4 Hz, observed for a signal with lower η value can be described to the carbon atom of cyano group placed closer to fluorine substituent. Having NOE data and the values of relaxation time T_1 (C13 – 12.2 s, C12 – 13.6 s, C protonated – 1.57 s) and assuming isotropic reorientation of the molecule the distance C13–H8 has been estimated to be 2.40 Å. The determined value is satisfactorily close to that found from crystallographic data (2.56 Å) as well as to that calculated using semi-empirical AM1 method implemented in HyperChem 4 program (2.57 Å). This supports our expectation that the structure of **2** in solution is similar to that in a solid state.

Because of excellent agreement between the values of the above mentioned distance obtained from crystallography and from semi-empirical calculation it was decided to elucidate the structures of compounds **1** and **3** using the latter method. The calculations revealed that the molecule of compound **1** is planar whereas the central ring of molecule of **3**, similarly as that of **2**, has a boat-like structure. For both compounds, **1** and **3**, one of ^{5}J(CN,F) coupling constants is small but measurable and the other is equal to zero. The values of the discussed coupling constants are collected in Table 1 together with the distances between coupled nuclei calculated by AM1 method. We are inclined to believe that in all the compounds investigated, the higher values of ^{5}J(CN,F) concern the *Z*-CN groups rather than the *E* ones and that this reflects the participation of the 'through-space' mechanism in this coupling. However, because of small values of ^{5}J(CN,F) and the lack of correlation between these values and C–F distances, one should be careful to draw too many far reaching conclusions.

Table 1 Spin-spin coupling constants between fluorine and CN carbon atoms in investigated compounds

Compound	^{5}J(C,F) *E*-CN	 *Z*-CN	*d*(*Z*-CN-F)^a Å
1	0	~1	2.685
2	1.2	2.4	2.350
3	0	1.2	2.211
4	1.5	18.8	2.661
5	0	13.7	2.766

^{a} Determined by AM1 method.

Table 1 also gives the values of ^{5}J(C,F) coupling constants for compounds **4** and **5**. The structures of those compounds are similar to that of **1** but in this case the electrons of C–H bonds can participate in exchanging the information about spin states. The 'through-space' mechanism of C,F coupling is here more evident. It is striking that the values of ^{6}J(H,F) coupling constants are 0 and 1.0 Hz for *E*-CH_3 and 7.2 and 8.0 Hz for *Z*-CH_3 in **4** and **5**, respectively. Thus, also the methyl protons – fluorine coupling in these compounds apparently involves "through-space" non-bonding electron interaction. Our findings confirm that the interpretation of even smaller C,F coupling constants involving 'through-space' mechanism can provide a useful hint in structural studies.

Crystal data for 2: $C_{18}H_9FN_2O$, M =288.27, orthorhombic, space group $P2_12_12_1$ (no. 19), ρ 1.375 Mg/m^3, Z = 4, a = 7.6238(17) Å, b = 11.970(3) Å, c = 15.262(3) Å, V = 1392.7(5) Å^3, T = 293(2) K, MoKα radiation (λ = 0.71073 Å), μ = 0.096 cm^{-1}, Siemens P3 diffractometer, $2\theta_{max}$ = 50°, ω–2θ scan. 2876 reflections were collected (2446 unique, R_{int} = 0.0140) which were used in all calculations. Absorption correction based on the crystal shape was applied. The structure was solved by direct methods[26] in $P2_12_12_1$ space group and was refined by full-matrix least-squares on F^2.[27] All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were located using difference Fourier maps and isotropically refined. Refinement converged at wR_2 = 0.0772 for 2446 data and 236 parameters (R_1 = 0.0289 for 2303 unique reflections with $I > 2\sigma(I)$). Absolute structure could not be determined reliably due to the high e.s.d. for the refined Flack x parameter 0.6(10).[28] Residual electron density = +0.17/–0.09 e Å^{-3}. Atomic co-ordinates, displacement parameters, bond lengths, bond angles and torsion angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC).

Techniques used: ^{1}H and ^{13}C{H} NMR

References: 29

Scheme: 1

Tables: 8

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