Theoretical Study on the Molecular Geometries of Substituted Fluoroforms

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Z. Naturforsch. **37a**, 134–138 (1982); received December 15, 1981

The F ... F non-bonded distances are strikingly constant in a large series of trifluoromethyl derivatives. Semiempirical NDDO calculations have been performed for five representative molecules. From the energy partitioning it appears that the bonding interactions (resonance energy terms) are dominating in determining the molecular geometry. The constancy of the non-bonded distances may occur as the changes in the bond lengths and bond angles are compensated. A good description of the total energy, however, necessitates the inclusion of the two-center electrostatic terms of all atom pairs.

Introduction

The concept of intramolecular non-bonded interactions has proved to be very useful [1, 2]. For example, the geminal F...F non-bonded distances as determined experimentally, appear to be strikingly constant. Their mean value in a series of 40 CF_3 derivatives was found to be 2.162 Å with a standard deviation of 0.008 Å [3]. Further recent results are in complete agreement with this observation. Thus, e.g., this distance is 2.151, 2.157, 2.153 Å in CF_3Cl, CF_3Br, CF_3I, respectively [4a]; 2.160, 2.163, 2.153 Å in F_3CSF, F_3CSCl, $(F_3C)_2S$, respectively [4b]; 2.167 Å in CF_3CH_2F [4c]; 2.161 Å in CF_3CHF_2 [4d]; 2.168 Å in $(CF_3)_4Sn$ [4e]; 2.159 Å in $C_6H_5CF_3$ [4f]; 2.152 Å in $(CF_3)_4Ge$ [4g]; 2.148 Å in $C(CF_3)_4$ [4h]; 2.159 Å in $(CF_3)_2Hg$ [4i]. The observation on the constancy of the F...F distance has been successfully used in discussing controversial structural results [3, 5]. The constancy of the O...O non-bonded distances in sulphone molecules has also been noted [6] and this observation has been utilized, among others, in assigning rotational spectra (cf., e.g. [7]). Glidewell and Meyer [5] have recently carried out MINDO/3 calculations for *gem*-dihalides and related molecules, H_2CY_2. The constancy of the Y...Y distances has again been observed and it was proposed that the Y...Y non-bonded distance represents the limiting Y...Y contact determining the C—Y bond length for a given bond angle Y—C—Y.

Surveying the literature reveals that relatively little effort has been spent on understanding the *origins* of the constancy of non-bonded distances in large series of molecules. Thus the present work on some trifluoromethyl derivatives has been initiated. The primary aim was to throw some light on the relative importance of the bonded and non-bonded interactions in determining these molecular geometries.

The energy partitioning has been carried out for the calculations in which the experimentally determined geometries have been *assumed*. To test the calculations, however, complete geometry optimization was performed for fluoroform. This test showed good agreement between the experimental and calculated geometries. Even if the experimental and calculated structures would be somewhat different, however, it is expected that the differences have systematic character and do not influence the conclusions of the energy partitioning.

It is pleasing that the calculated parameters were consistent with the experimental information where available, but the choice of the molecules for the calculations was made on the basis of the simplicity of these molecules and not on that of the level of accuracy of their experimental geometries. This

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may be justified by the fact that the experimentally observed constancy of the F...F distances referred to a relatively large series of derivatives.

Method

The quantum-chemical calculations have been performed by the semiempirical NDDO method [8, 9], used in the same version as in [10]. The total energy partitioning was carried out according to Fischer and Kollmar [11] as described for the NDDO version by Köhler and Birnstock [9].

The total energy is the sum of one- and two-center terms:

$$E_t = \sum_A E_A + \sum_{A \neq B} \sum E_{AB},$$

where

$$E_A = E_A^J + E_A^V + E_A^K.$$

The one-center terms are in turn the electron-electron repulsion, the electron-nuclear attraction and the exchange energy. The two-center part is given in the form of the following sum:

$$E_{AB} = E_{AB}^R + E_{AB}^J + E_{AB}^V + E_{AB}^N + E_{AB}^K,$$

where E_{AB}^R is the resonance energy and E_{AB}^N the nuclear-nuclear repulsion. The other terms are the two-center equivalents to the corresponding one-center terms. The following notations are used:

$$E_A^{ES} = E_A^J + E_A^V \quad \text{and}$$

$$E_{AB}^{ES} = E_{AB}^J + E_{AB}^V + E_{AB}^N,$$

defining the sum of the classical Coulomb terms as one-center and two-center electrostatic terms.

The calculations for the five trifluoromethyl derivatives considered have been performed using experimental geometries: fluoroform CF_3H [12], 1,1,1-trifluoroethane CF_3-CH_3 [13a]*, 3,3,3-trifluoropropyne (trifluoromethylacetylene)$CF_3C\equiv CH$ [14], 3,3,3-trifluoropropene $CF_3-CH=CH_2$ [15], and trifluoromethyl hypofluorite CF_3-OF [16].

Previous NDDO results on NH_3 and NF_3 [17], as well as on trans- and cis-glyoxal [10] are also considered in the discussion.

For the CF_3H molecule the C—F and F...F distances have been optimized and the dependence of the partitioned energy terms on the C—F and F...F distances has been examined. The C—H distance has also been optimised and the experimental value (1.098 Å) was reproduced within 0.01 Å.

Results and Discussion

First the relative magnitudes of the energy terms of bonded and non-bonded atom pairs within the CF_3 groups are considered. The two-center repulsive and attractive terms for the C—F and C—X bonds (X denotes the atom connected to the CF_3 group) and for F...F atom pairs are collected in Table 1 together with the same terms for the corresponding interactions in NH_3, NF_3, and trans- and cis-glyoxal.

The repulsive and attractive terms are larger for the F...F pairs of atoms than for the C—F bonds in the trifluoromethyl derivatives. This situation is just the reversed to what is generally observed. In most cases, the electron-electron repulsion, the nuclear-nuclear repulsion and the absolute value of the electron-nuclear attraction are larger for the bonded than for the non-bonded atom pairs. The sum of the repulsive and attractive term, i.e. the electrostatic terms is several tenths of a.u. for bonded atom pairs. The total is positive, i.e. the repulsion dominates. For the non-bonded pairs, the electrostatic term is of the magnitude of thousands of a.u. A typical example is presented by NH_3 in Table 1. For NF_3 the F...F terms come close to the corresponding N—F terms. For cis-glyoxal the corresponding terms are larger than for trans-glyoxal. The examples shown demonstrate that the presence of electronegative atoms at short distances in a molecule increases the relative magnitude of non-bonded repulsive and attractive terms. In these four examples, with the exception of the E_{AB}^N value of trans-glyoxal, the bonded interactions have larger values, than the non-bonded terms. It should be emphasized that the electrostatic term is in each case by two orders of magnitude larger for the bonded atom pairs than for the non-bonded ones.

The two-center resonance, electrostatic, and exchange terms of the CF_3Y molecules are shown in Table 2. Comparison of the partitioned energy terms in various derivatives may be of interest. Very small

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* The referee pointed out a more recent and more accurate work on CF_3-CH_3 [13b]. The geometries of the CF_3 groups, however, differ very little in the two studies.

Table 1. Two-center electrostatic energy terms, a.u.

Molecule	E^{J}_{C-F}	E^{J}_{C-X}	$E^{J}_{F...F}$	E^{V}_{C-F}	E^{V}_{C-X}	$E^{V}_{F...F}$	E^{N}_{C-F}	E^{N}_{C-X}	$E^{N}_{F...F}$
CF_3-H	9.4598	1.4897	12.3131	−20.2531	−3.2110	−24.2780	11.1236	1.9278	11.9704
CF_3-CH_3									
staggered	9.4369	4.7297	12.4311	−20.2146	−10.0540	−24.4359	11.0986	5.5338	12.0114
$CF_3-C\equiv CH$	9.3056	4.9302	12.4499	−20.0837	−10.4635	−24.4855	11.0986	5.7833	12.0421
$CF_3-CH=CH_2$	9.3492	4.8734	12.4380	−20.0602	−10.3125	−24.4355	11.0161	5.6709	12.0044
CF_3-OF	9.2653	7.4766	12.3073	−20.1459	−16.2991	−24.3461	11.2333	9.1040	12.0434
	E^{J}_{N-X}		$E^{J}_{X...X}$	E^{V}_{N-X}		$E^{V}_{X...X}$	E^{N}_{N-X}		$E^{N}_{X...X}$
NH_3	2.2150		0.2635	−4.5240		−0.5605	2.5295		0.3010
NF_3	13.2346		13.0163	−27.8108		−25.9689	14.9361		12.9578
	$E^{J}_{C=O}$	E^{J}_{C-C}	$E^{J}_{O...O}$	$E^{V}_{C=O}$	E^{V}_{C-C}	$E^{V}_{O...O}$	$E^{N}_{C=O}$	E^{N}_{C-C}	$E^{N}_{O...O}$
trans-glyoxal	9.3921	5.0305	5.6365	−19.3087	−10.3688	−11.1420	5.3244	5.5519	5.5068
cis-glyoxal	9.3807	5.0316	7.0878	−19.3017	−10.3694	−13.9475	10.5220	5.5519	6.8636

Table 2. Two-center energy terms of CF_3Y-type molecules, a.u.

Y	E^{R}_{C-F}	E^{R}_{C-X}	$E^{R}_{F...F}$	E^{ES}_{C-F}	E^{ES}_{C-X}	$E^{ES}_{F...F}$
H	−1.1787	−0.7437	0.0149	0.3303	0.2065	0.0055
CH_3	−1.1544	−1.1122	0.0154	0.3210	0.2094	0.0067
$C\equiv CH$	−1.1512	−1.2438	0.0158	0.3205	0.2500	0.0065
$CH=CH_2$	−1.1347	−1.1806	0.0154	0.3051	0.2318	0.0068
$O-F$	−1.2039	−1.1121	0.0162	0.3526	0.2814	0.0047

Y	E^{K}_{C-F}	E^{K}_{C-K}	$E^{K}_{F...F}$	E_{C-F}	E_{C-X}	$E_{F...F}$
H	−0.3112	−0.2769	−0.0060	−1.1596	−0.8141	0.0145
CH_3	−0.3020	−0.2956	−0.0060	−1.1354	−1.1984	0.0161
$C\equiv CH$	−0.3002	−0.3190	−0.0061	−1.1310	−1.3128	0.0162
$CH=CH_2$	−0.2979	−0.3054	−0.0059	−1.1274	−1.2542	0.0164
$O-F$	−0.3136	−0.2999	−0.0062	−1.1650	−1.1306	0.0147

deviations are seen in the molecules with carbon as adjacent atom to the CF_3 group while the largest deviation from the mean occurs for CF_3OF.

In order to determine the role of bonded and nonbonded interactions, the behaviour of the energy terms as a function of the C—F and F...F distances is investigated. The geometry of CF_3H has been optimized, the total energies and their one-center and two-center parts for different C—F and F...F distances are shown in Table 3. It can be seen that the total-energy minimum occurs at $r_{F...F} = 2.146$ Å for $r_{C-F} = 1.33$ Å (the experimental value). For the experimental $r_{F...F}$ value (2.166 Å) $r_{C-F} = 1.34$ is obtained (giving slightly higher total energy minimum). Thus the calculations well reproduce the experimental geometry.

The partitioned energy terms as a function of the F...F distances for $r_{C-F} = 1.33$ Å are shown in

Table 3. Energy terms of CF_3H, a.u.

r_{C-F} Å	$r_{F...F}$ Å	E_t	$\sum_{A} E_A$	$\sum\sum_{A \neq B} E_{AB}$
1.32	2.106	−87.2785	−83.0580	−4.2205
	2.116	−87.2791	−83.0563	−4.2228
	2.126	−87.2795	−83.0552	−4.2243
	2.136	−87.2794	−83.0531	−4.2263
	2.146	−87.2790	−83.0515	−4.2275
	2.166	−87.2769	−83.0483	−4.2286
1.33	2.116	−87.2791	−83.0714	−4.2077
	2.136	−87.2802	−83.0683	−4.2119
	2.146	−87.2804	−83.0668	−4.2136
	2.156	−87.2801	−83.0652	−4.2149
	2.166	−87.2795	−83.0637	−4.2158
	2.176	−87.2785	−83.0622	−4.2163
	2.186	−87.2770	−83.0607	−4.2163
	2.196	−87.2751	−83.0592	−4.2159
	2.216	−87.2694	−83.0562	−4.2132
1.34	2.156	−87.2790	−83.0823	−4.1967
	2.166	−87.2793	−83.0787	−4.2006
	2.176	−87.2788	−83.0772	−4.2016

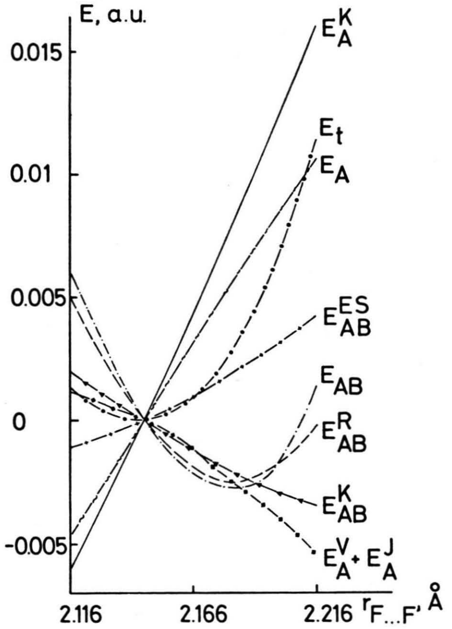

Fig. 1. Total energy and the partitioned energy terms as a function of $r_{F...F}$ for $r_{C-F} = 1.33$ Å. For notation see Text.

Figure 1. The energy values refer to the most stable state ($r_{F...F} = 2.146$ Å). It can be seen that the one-center part of the total energy monotonously increases with increasing F...F distance, the two-center term, on the other hand, has a minimum at 2.186 Å. The further partitioning of the two-center term demonstrates that only the resonance energy curve shows minimum at the same distance as the two-center term.

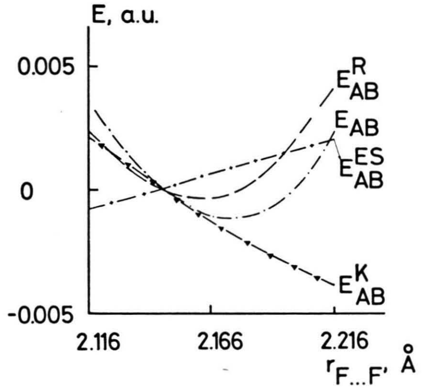

Fig. 2. Contributions of the bonded atom pairs to the two-center energy and its partitioned terms as a function of $r_{F...F}$ for $r_{C-F} = 1.33$ Å.

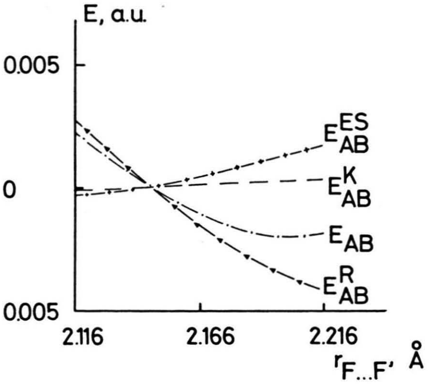

Fig. 3. Non-bonded contributions corresponding to the bonded energy terms of Figure 2.

Finally the partitioning of the two-center terms into bonded and non-bonded contributions is considered. Figures 2 and 3 show the bonded and non-bonded contributions, respectively. Among the bonded terms, only the resonance energy curve has a minimum at 2.166 Å, the sum of the two-center bonded terms shows a minimum at 2.176 Å. None of the non-bonded component terms have minima, while their sum has a flat minimum at 2.206 Å.

It can be concluded that the bonded interactions, especially the resonance terms, are primarily determining the molecular geometry. The fact, however, that the minimum of the E^R_{AB} (bonded) curve is not exactly at the same F...F distance as that of the total energy curve, points to the fact that the former is not exclusively responsible for the actual geometry. The total energy curve can be best approximated by the sum of the E^R_{AB} (bonded) and E^{ES}_{AB} curves. Only the addition of the *complete* electrostatic contribution reproduces well the total energy curve, while the inclusion of only selected bonded or non-bonded terms does not give acceptable results. It seems therefore that the additional effect to the resonance energy comes from contributions of all atom pairs. Since the two-center electrostatic terms are for each atom pair positive, the net electrostatic potential is of repulsive character.

As the bonded interactions appear to be primarily determining the geometry in the series of molecules examined, the constancy of the F...F distances may be a consequence of compensated changes in the C—F bond lengths and F—C—F bond angles.

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