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The Trifluoroacetato (CF₃COO—) and Trifluoroacetate (CF₃COO[−]) Groups, their Conformation from a Database Survey of Crystal Structures and *Ab Initio* MO Calculations

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Abstract

Data for structures involving either of these groups have been drawn from the Cambridge Structural Database and divided into bidentate and monodentate categories. Statistical distributions of bond distances, selected bond and torsion angles from 414 groups contained in 194 structures yield the following mean values (with e.s.d.'s): C—F = 1.29 (6), C—C = 1.53 (4), C—O (bidentate) = 1.24 (5), C—O— (monodentate) = 1.25 (4), C=O (monodentate) = 1.21 (4) Å. Angles in the CF group vary widely from the expected threefold symmetry (e.s.d. of distribution 8.8°). Torsion angles F—C—C—O for the bidentate groups range fairly evenly over all possible values, suggesting free internal rotation. Among monodentate groups all values of the torsional angles are possible but with a marked preference for a C—F to eclipse the carbonyl C=O bond. These observations show good agreement with the results of *ab initio* calculations using GAUSSIAN90. The calculated barrier to rotation for the bidentate (ion) form of the group is only 310 J mol^{−1} and for the monodentate form (as in the acid) 2.55 kJ mol^{−1}.

Introduction

Examination of the Cambridge Structural Database (CSD) at 1.9.92 revealed references to 186 structures involving trifluoroacetato groups and 42 references to trifluoroacetate groups. For the purpose of this investigation these 228 structures were treated together and the abbreviation TFA implies both types of group. Coordinate data is available for 194 of these references and the work is based on these, containing a total of 414 TFA groups. A list of the CSD reference codes of these is given in Table 3.*

The TFA group was selected for detailed study because it had been noticed that there was exceptionally wide disparity in the molecular parameters from different reported structures. Problems frequently occur in the location of F atoms, at the worst they may not be found at all. Torsion angles relating the CF₃ and carboxyl groups are often not explicitly reported, but when calculated

* A full list of references with compound names and CSD codes has been deposited with the IUCr (Reference: LI0176). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

from the published coordinates a wide variation is found. There are no chemical reasons why the CF_3 group should deviate from approximate threefold symmetry, yet the observed deviations are considerable; in five extreme cases, the published coordinates when plotted reveal a quite improbable situation whereby the four atoms attached to the central carbon of the CF_3 group all lie on one side of a plane through the carbon. Reference back to the original papers in such extreme (reflex) cases invariably reveals low-accuracy structure determination. Often disorder is reported in publications (very high U_{ij} values), but is very rarely allowed for.

In many of the relevant structures the TFA group is used as a ligand to medium or heavy metal atoms which dominate the observable X-ray scattering, reducing the proportional contribution from the disordered F atoms to the measured intensity, thereby contributing to the problem of atom location.

The electron-density spread of the F atoms in CF_3 may be observed in some suitable instances. In the case of the complex of mercury(II)trifluoroacetate and pyridine oxide (Halfpenny & Small, 1991), the plane of the three F atoms is approximately parallel to (010) which facilitates the plotting of sections of the electron-density map. The contours in Fig. 1(a) show the difference electron density obtained using the parameters for the final determination with the three F atoms omitted ($R = 0.078$). Inclusion of anisotropic F improves R to 0.022, but only partially allows for the crescent-shaped electron distribution leaving residual density in intermediate positions, Fig. 1(b). Inclusion of further partial F atoms at these sites would improve R to 0.019 and lead to a disordered model which might be described as partial occupation of two sets of positions, whereas the true picture would be extreme libration (hindered rotation) of CF_3 .

The objective of the first part of the investigation was to establish the most probable model of the TFA group, bearing in mind the likelihood of fairly free rotation of CF_3 . The second part was to perform an *ab initio* molecular orbital calculation, using the best possible basis set, of the molecular parameters for comparison with the results of the first part.

Procedure

The Cambridge Structural Database was searched using the facilities of the Chemical Database Service at Daresbury SERC laboratory. Using the program *CSSR* (Crystal Structure Search Retrieval), a file containing all references with the words trifluoroacetato, trifluoroacetate and trifluoroacetic was produced; for each reference the program *CRAD* (Crystal Radial Distribution) was used to establish the coordination around the metal atom (where present) and the TFA groups designated as bi- or monodentate. Bidentate groups were identified as those in which both O atoms were bound to a metal atom (not

necessarily the same one) at more or less equal distances (within 0.1 \AA), whereas monodentate groups had only one O atom bound primarily to a metal, sometimes the second oxygen of the monodentate group was also bound to a metal but at an appreciably greater (0.3 \AA) distance. In bidentate groups both oxygens were considered to be equivalent from the point of view of bonding. In the monodentate TFA groups the carbonyl ($\text{C}=\text{O}$) oxygen was identified as the one not primarily coordinated to the metal atom. Observed bond length differences between $\text{C}=\text{O}$ and $\text{C}-\text{O}-$ were found to be unreliable in this respect, as will be discussed later. Of the 414 groups available 173 were considered to be monodentate and 241 bidentate.

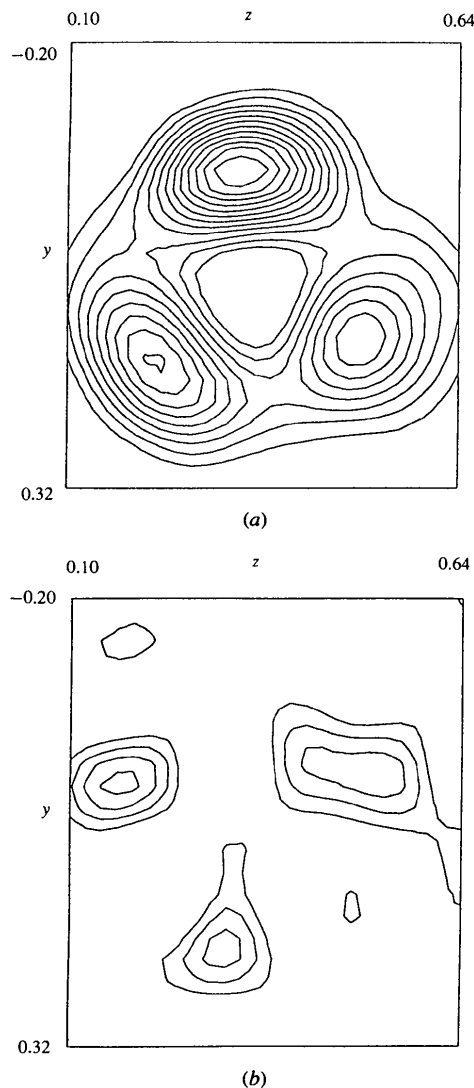


Fig. 1 (a) Section of ΔF map at $x = 0.38$ for pyridine oxide mercury(II) trifluoroacetate complex with F atoms omitted from F_{calc} ($R = 0.078$). Electron density is in the approximate plane of the F atoms. (b) As in Fig. 1(a), but with anisotropic F atoms included in F_{calc} ($R = 0.022$). Showing residual intermediate peaks.

The database coordinates were transferred to the Lancaster University Sequent Symmetry computer, molecular geometry calculations made use of the program *XANADU* (Roberts & Sheldrick, 1975). In addition to the bond distances C—F, C—C and C—O, the dihedral angles between the planes CCF and CCOO were calculated.

If *A*, *B* and *C* are the observed dihedral angles between the mean plane CCOO and the three CCF planes, then the mean torsion angle τ between the C—F and the C—O bonds in each TFA group may be defined and calculated as follows.

(a) When the two C—O bonds are to be regarded as equivalent (a bidentate group) so that if CCOO has the expected symmetry *mm* (2_v) and CF₃ has the expected symmetry *3m* (3_v), the mean F—C2—C1—O torsion angle τ (Fig. 2) will have unique values between 0 and 30°, where $\tau = 1/3(A + C - B)$ with $A < 30^\circ$ and $B < 60^\circ$. Ideally, if the symmetries were exact, $A = \tau$, $B = 60 - \tau$, $C = 60 + \tau$.

(b) When O1 and O2 are not equivalent (as in the monodentate structures), CCO1O2 then has only *m* symmetry and CF₃ *3m* (3_v) symmetry; the possible range of τ (relative to C=O) is 60° and $\tau = 1/3(A + C - B)$ or $\tau = 60 - 1/3(A + C - B)$ depending upon the C=O direction, the decision being made from a plot of the TFA group projected onto a plane perpendicular to C—C which can be output by *XANADU*.

In general, coordinates were taken from CSD, but whenever unusual features were apparent (reflex angles, anomalous distances or symmetrical CF₃ groups) reference was made to the original papers. Structures with reflex angles were excluded from the analysis. The values of the distances and angles were grouped into convenient ranges and a number within each range of values plotted against the midpoint of each range. The distributions are shown in Figs; 3(a)–3(e), 4(a), 4(b), 5, 6 and 10. Mean values, e.s.d. and extreme values of the distributions of the bond distances and dihedral angles of the TFA group are given in Table 1.

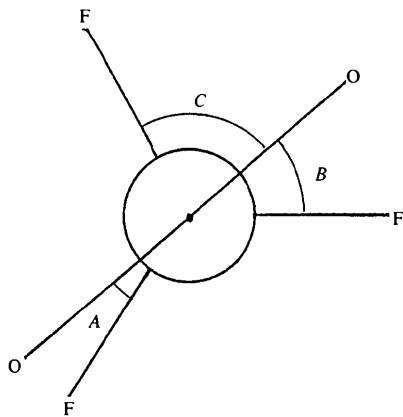


Fig. 2. Defining the dihedral angles *A*, *B* and *C*.

Table 1. Summary of results of data analysis

	(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)
F—F angle projected	414	1242	83.9	177.3	120.0	8.8		
C—F distance	414	1242	1.052	1.604	1.292	0.057	1.350	1.363
							1.350	
							1.338	
C—C distance	414	414	1.341	1.728	1.530	0.041	1.537	1.559
C—O distance bidentate	241	482	1.116	1.470	1.242	0.053		1.254
C—O— distance monodentate	173	173	1.130	1.343	1.250	0.037	1.343	
C=O distance monodentate	173	173	1.061	1.380	1.213	0.038	1.212	

Key: (a) number of groups, (b) number of values, (c) least value, (d) greatest value, (e) mean value, (f) e.s.d. of distribution, (g) and (h) values from *ab initio* calculations, (g) monodentate, (h) bidentate.

Discussion

Distances

As expected, the molecular dimensions reported for the TFA group show an unusually wide variation, as shown in Figs. 3–6 and Table 1. Of the bond distances, C—F values show the greatest variability (1.05–1.60 Å), Fig. 3(a). There appears to be no chemical reason for such variation, which must therefore be attributed to inaccuracy in the location of the F atoms. The mean distance for this distribution, C—F = 1.29 Å, has an e.s.d. of 0.06 Å. The other bond distances in the TFA group exhibit only slightly less variation, which may be due to the effect of F positional uncertainty on the group as a whole. The C—O distances call for comment. In bidentate TFA groups the two C—O distances would be expected to be approximately equal. The range of differences in the two C—O values for reported structures is shown in the distribution Fig. 4(b), where it will be apparent that the differences although widely ranging are grouped around zero. In the monodentate groups, the difference between the lengths of C—O— and C=O in each TFA group would be expected to be quite large (0.15 Å), corresponding to the difference between normal single- and double-bond distances. The distribution of these differences is shown in Fig. 4(a); in 30 out of 173 groups the C=O bond is reported to be longer than C—O— and the mean and most probable values of the differences are less than the expected value. As it is unlikely that either of these features is of meaningful chemical significance, there must be unexpectedly large errors in the O and C positions. Such large errors could arise (a) from the influence of very large uncertainties in F-atom positions upon the whole TFA group or (b) from absorption errors and series termination errors arising from incomplete data sets which affect atom positions near even moderately heavy atoms.

Angles

The distribution of the F—C—F angles projected along the C—C bond onto a perpendicular plane is given

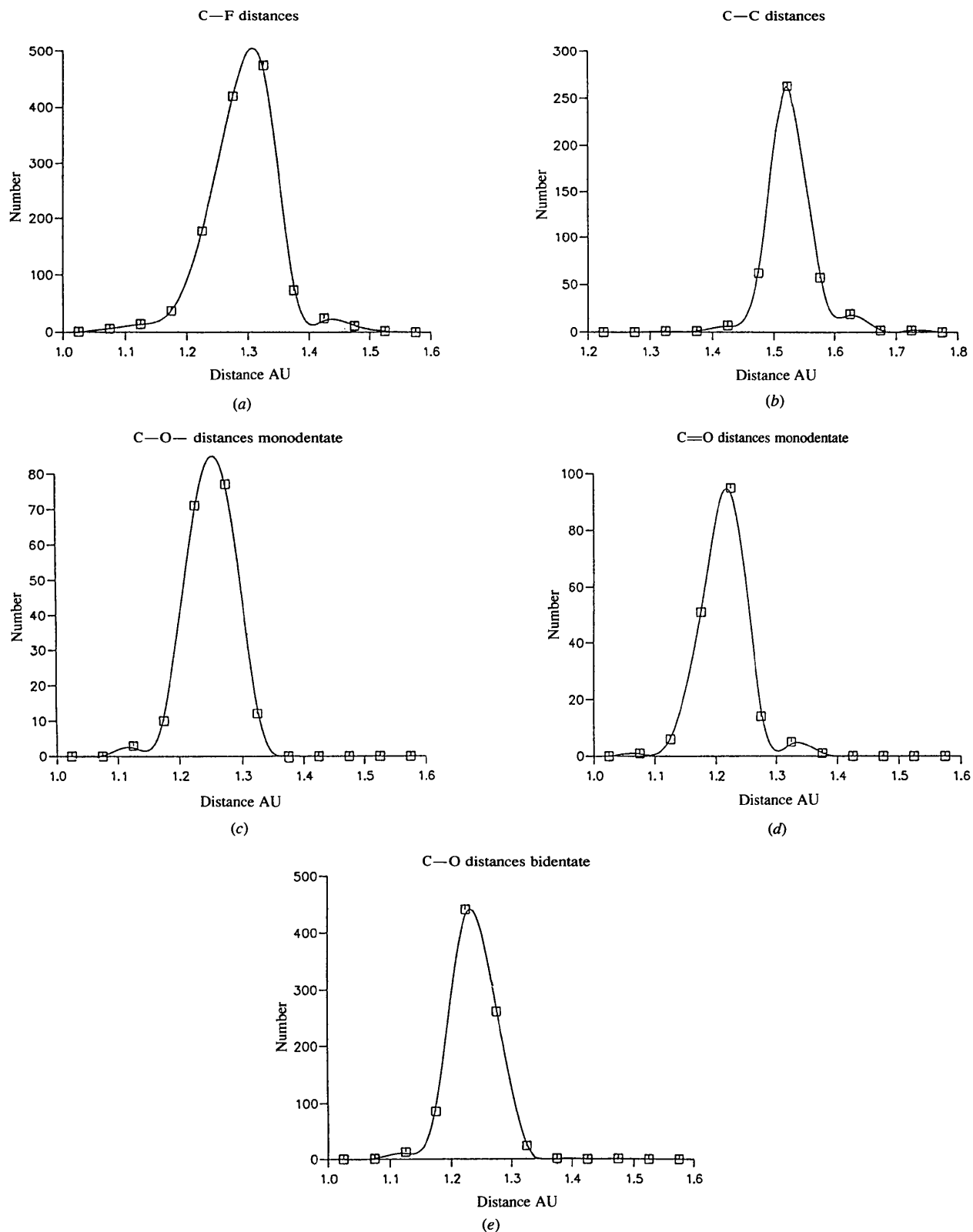


Fig. 3. Distribution curves for observed distances in TFA groups showing the number of distances within each range versus the midpoint of each range. (a) C—F, (b) C—C, (c) C—O— monodentate, (d) C=O monodentate and (e) C—O bidentate.

in Fig. 5 and Table 2. Because the sum of the angles in each group is 360°, the mean value is necessarily 120°. It will be noted that the range of values is wide (some of the more extreme cases, *e.g.* where the angle is greater than 180°, have been omitted), and the standard deviation of the distribution (8.8°) corresponds to an e.s.d. of 0.20 Å in the azimuthal position of the F atoms, *i.e.* approximately four times the error of the radial position. This gives a strong indication that the positional errors of F arise from a rotational uncertainty of the CF₃ group. The torsion angles as previously defined for the bidentate and monodentate cases are shown in Figs. 6 and 10, where the angles are grouped in 5° intervals. In the 241 bidentate groups where the two O

atoms are equally bound to metal atoms or the group is ionic, the possible angles are confined to the range 0–30° (Fig. 6); all angles appear possible. When the monodentate groups are considered, the torsional angle is expressed relative to the carbonyl C=O direction (identified by O not bonded to a metal), the range of possible values becomes 0–60° and the histogram, Fig. 10, shows that all values are possible but there is a preference for C=O rather than C—O— to eclipse a C—F bond.

The only symmetry possible in the TFA group is a mirror plane, and two situations can arise. The plane of symmetry must contain both C atoms and one F, but the O atoms can either both lie in that plane, case A, or across the plane being symmetry related, case B Fig. 7.

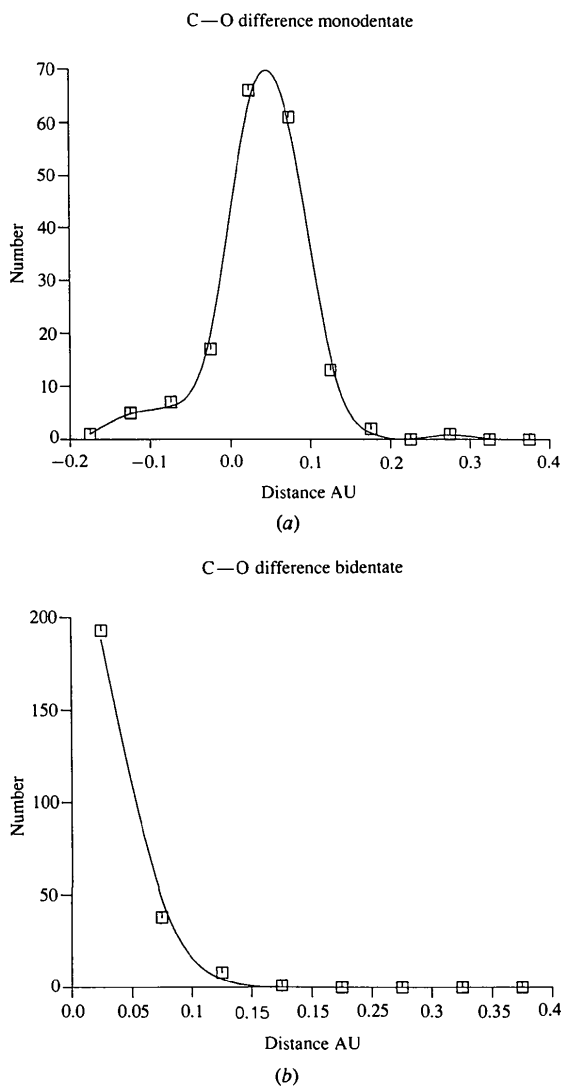


Fig. 4. (a) Distribution curve for differences between C—O— and C=O distances in each TFA group for monodentate structures. (b) Distribution curve for magnitude of differences in C—O distances in each TFA group for bidentate structures.

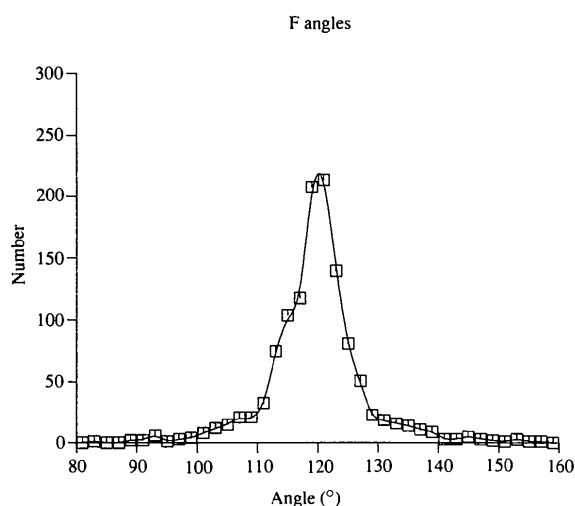


Fig. 5. Distribution of F—C—F angles projected along C—C, showing deviations from threefold symmetry.

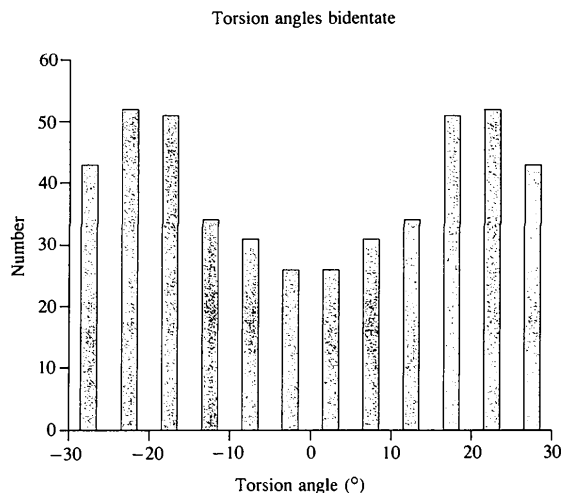


Fig. 6. Distribution of torsion angles, τ , for bidentate structures.

Table 2. ΔH_f optimized energies from MP2 versus Energy calculations
torsion angle τ

(a)	HTFA
τ ($^\circ$)	ΔH_f (kJ mol $^{-1}$)
0	-1380187.23
15	-1380186.94
30	-1380186.13
45	-1380185.18
60	-1380184.68
(b)	TFA (anion)
τ ($^\circ$)	ΔH_f (kJ mol $^{-1}$)
0	-1378636.83
15	-1378636.67
30	-1378636.52

Examples of both of these cases are found, six of type A (Dawans, Dewailly, Meunier-Piret & Piret, 1974; Chih & Penfold, 1973; Faggiani, Johnson, Brown & Birchall, 1979), two of which occur in the same crystal structure (Faggiani, Johnson, Brown & Birchall, 1978), and five of type B (Kaas & Springborg, 1986; Bruno, Lo Schiavo, Rotondo, Piraino & Faraone, 1987), three of which are in the same crystal structure (Harrison, Giorgiotti & Bunzli, 1985). Type B is necessarily bidentate with $t = 30^\circ$. Among the six type A cases, five have $t = 0^\circ$ (i.e. with C=O eclipsed by F) and one $t = 60^\circ$.

In only one reported structure refinement does it appear that a CF₃ group with constrained threefold symmetry was assumed (Alyea, Dias, Ferguson & Siew, 1984).

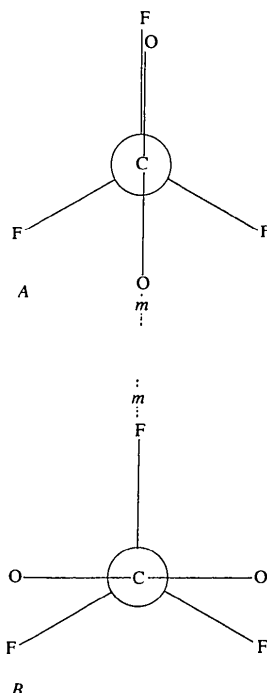


Fig. 7. Symmetry possibilities in the TFA group.

The GAUSSIAN90 *ab initio* package (Frisch *et al.*, 1990) was used to optimize the structures of the trifluoroacetate anion (TFA) and trifluoroacetic acid (HTFA). It was expected that these two situations would correspond approximately to the structures comprising the bidentate and monodentate abstracted data sets, respectively. The structures were obtained at the $MP2 = \text{Full}/6-31+G^{**}/MP2/6-31+G^{**}$ basis set and correlation energy levels. The anion, due to space limitations, was run at the $MP2 = \text{Full}/6-31G^{**}$ level. Although of good quality the basis set still requires augmentation for these difficult systems. The optimized structures for the two cases are shown in Figs. 8 and 9. The barriers to rotation were obtained by reoptimizing the structures for fixed twist angles. In the case of the anion TFA, the barrier to rotation is negligible,

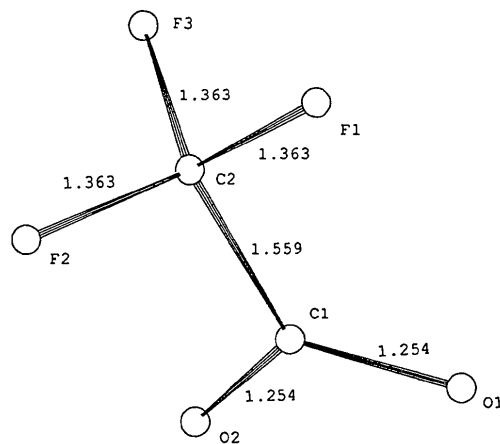


Fig. 8. Principal optimized distances (Å) in MP2 model of the TFA anion.

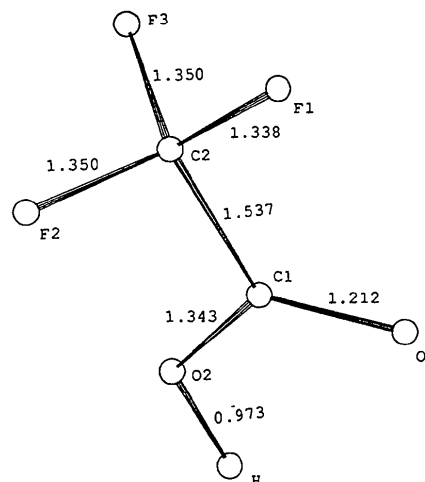


Fig. 9. Principal optimized distances (Å) in MP2 model of HTFA acid.

310 J mol⁻¹, *i.e.* the system is essentially a free internal rotor with no preferred orientation of CF₃ relative to the COO group. The barrier to rotation for the acid HTFA is an order of magnitude greater, although still low in absolute terms, the Hartree-Fock barrier is 4.07 kJ mol⁻¹, whereas at the MP2 correlated level the barrier falls to 2.55 kJ mol⁻¹. This value is to be compared with that reported by Stolwijck & van Eijck (1985) of 2.89 kJ mol⁻¹ obtained from microwave studies. The difference (0.34 kJ mol⁻¹) from the MP2 value represents extremely good agreement between the two investigations. The previous 4-31G and 6-31G** studies of Lawrey (1989) give values in excess of 4.2 kJ mol⁻¹, for the barrier. In HFTA the conformation of lowest energy is with a F atom eclipsed by the carbonyl O atom, the highest energy form being 180° away. This is shown in Fig. 10 where the energy curve from Table 2 is plotted for an extended series of angles of twist, also plotted on the same diagram as are the results from the data survey, of the frequency of occurrence of ranges of angles of rotation. The observed data correlates satisfactorily with the theoretical energies.

The assumption has been made that replacing H in HFTA by a metal to give a monodentate complex would not essentially alter the situation in terms of the optimized structure. It is not feasible to perform the *ab initio* GAUSSIAN90 calculation using a metal, but the assumption may be checked at a lower level by a less precise calculation using the semi-empirical MNDO (Dewar & Thiel, 1977) method both on HTFA and on a model with Sn replacing H in HTFA. The minimum energy form in both cases was with an F atom eclipsing the carbonyl O atom. The semi-empirical barrier to rotation was equal in each instance (1.7 kJ mol⁻¹).

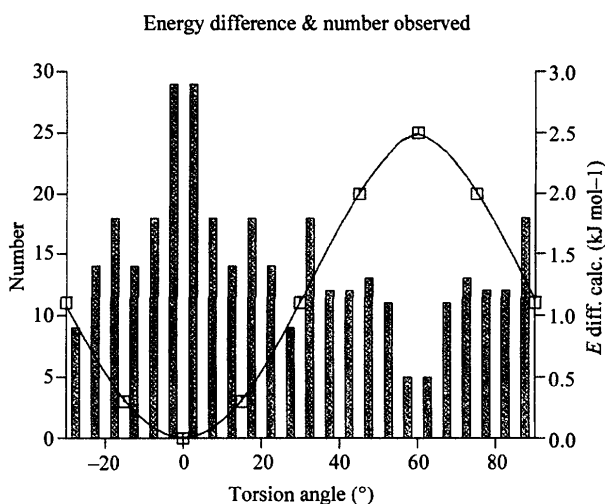


Fig. 10. Calculated energy differences for MP2 model of HTFA acid versus torsion angles [from Table 2(a), extended by symmetry]. Also plotted is the distribution of observed torsion angles for monodentate structures extended by symmetry.

Table 3. CSD reference codes

AMTFAC	ANTTFA	BAMNOS
BAMNUY	BANCIC	BANCIC1
BASBOM	BAVMUG	BAXLUH
BEGFEY	BENFIJ	BENFIJ1
BEYFIU	BICMUV	BIKTQE
BIKTUK	BINSOG	BITFOZ
BIVLOH	BIYPAA	BIZXEN
BODTOD	BODYEY	BODYEY1
BOFROD	BOKFAI1	BPFVAV
BUBCIP	BULMAW1	BULMEA1
BURTEN	BURTIR	BURTOX
BUTAGD	BUXTAP	CABMAT
CAHFIA	CAHKEB	CASMUE
CASWO11	CASWUO1	CATHIO
CAXHAK	CAZFEF	CEBRUW
CEXFUG	CEZBEO	CHFLAC
CIFGON	CIFNIO	CIFNOU
CILRIY	CINRIA	CIXBIU
CMCPRH1	COBVUK	COCXOH
CONVOQ	CONVOQ1	COXZYI
COZLE11	CPVFAC	CUNFOG
CUTJIK	CUVJOS	CUXYEZ
DAHWUE	DAJTUD	DAMTIU
DANBAV	DEDKIG	DEDKOM
DEPBIJ	DIBDEX	DOKNAS
DOYZOG	DUHVAD	DURWES
DUSRUE	EFASCO0	FABRYU1
FACAPR	FACCRE	FACFSB
FACMNA	FACMNB	FACMOB
FACMOC	FACMSN	FACPPT
FACRCP	FACUQNI	FAGHEA
FALCMO	FALDCW	FAMPMO
FATBOS1	FAVBEJ	FAVBIN
FAVJOB	FAVRID	FEKPIJ
FEZTIN	FIBGOM	FICJIK
FILJOZ	FITYIQ	FMABNI
FOFTID	FOKJOE	FUBLOD
FUBLUJ	FUHROP	FULCOE
FUNDAT	FUNDAT1	FUNDEX
FUNDEX1	FUNDIB	FUNDIB1
FUNDOH	FUNDOH1	GEBYIV
GELZOM	GEMWUO	GIJCEH
GITTUY	GOJJOE	HGFLAC1
HPTFAC	JABBET	JABBIX
JABMAA	JABMEE	JAYJUO
JEDUAO	JEPGOA	JICSIX
JIKHAM	KAKVUN	KARHIU
KAWRUV	KAYJYA	KAYNIH
KAYREH	KDFLAC	KELBUY
KHFLAC	KIBMIR	KIDLIS
KIDLOY	KIKDEN	KIPGAR
KIPGEV	MENFAD	MNYFAC
MOTFAC	MPITRZ	MPITRZ1
MSORHB	MSORHB1	OFACSN
OFACSO	OFAFSB1	PASFCO
PHGTFA0	PNPMOB	PNPMOC
PHGFAC	PTFAHG	SADREU
SECCOS	SECFUB	SEPVOY
SERVUG	SERYOD	SIMCIA
SIRKEJ	SITKOV	SIVZEC
TACTEW	TADZED	TAFACU
TFACMO	TFACUQ	TFAERH
TFALAH	TFAPCU	TFAPCU0
TMSNFA	TPFAHG	VILDID
VIMZIA	VIPNEN	

Concluding remarks

The GAUSSIAN90 calculation shows that there is a negligible barrier to internal rotation in the bidentate TFA group, the observed conformation in any structure will be a result of the intermolecular interactions. If a large enough group of structures are examined, an even distribution over all angles of rotation would be

expected, this is found to be the case. For the monodentate group (HTFA), the small but significant barrier to rotation predicted by the GAUSSIAN90 calculation would be superimposed on the intermolecular effects to give a distribution of angles favouring the minimum energy conformation. The database analysis is in agreement with this, indicating a bias towards the eclipse of the C—F bond by C=O rather than C—O—.

A comparison of the mean distances observed with those calculated indicates that, in general, the latter are always greater. Corrections for libration of the group as a rigid body and for internal rotation would increase the observed values, particularly the C—F distances. An unexplained feature is the shortening of the C—O— distance in monodentate structures compared with the calculated value. It will be of interest to investigate this feature in other carboxylic acid structures.

We acknowledge the use of the Cambridge Structural Database (Allen *et al.*, 1991) and of the EPSRC's Chemical Database Service at Daresbury.

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X-ray Studies on Crystalline Complexes Involving Amino Acids and Peptides. XXVIII. Recurrence of Characteristic Aggregation and Interaction Patterns in the Crystal Structures of DL- and L-Lysine Formate

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Abstract

The crystal structures of L-lysine formate [$P2_1$, $a = 5.431$ (1), $b = 7.546$ (1), $c = 12.095$ (2) Å, $\beta = 93.42$ (1)°, $Z = 2$] and DL-lysine formate [$P2_1/c$, $a = 10.205$ (2), $b = 11.152$ (2), $c = 8.491$ (1) Å, $\beta = 97.51$ (1)°, $Z = 4$] have been determined and refined to $R = 0.039$ and 0.054 for 1060 and 1689 observed reflections, respectively. Both the structures consist of alternating layers of unlike molecules. The aggregation pattern in the lysine layer in the L-lysine complex, with a straight and a zigzag head-to-tail sequence interconnecting the molecules, is almost the same as that observed in L-lysine acetate, L-lysine L-aspartate and L-lysine D-aspartate. In the DL-lysine

complex, hydrogen-bonded dimers of lysine are interconnected by head-to-tail sequences, as in DL-lysine hydrochloride. The structures thus demonstrate the relative invariance of certain aggregation and interaction patterns involving lysine. The relative invariance also extends to interactions between the side-chain amino group and the formate ions.

Introduction

We have been investigating the crystalline complexes involving amino acids and peptides in a long-range programme aimed at elucidating the atomic details of biologically and evolutionarily important non-covalent