were used. For conformation a, δ_x is 3.67; for b, δ_x is 3.92. Values of this magnitude are only consistent with coordination through the peptide nitrogen. With the knowledge that the unknown ligand is a cis nitrogen atom, a better calculation can be made using δ_{NH_2} from $Cu(en)(OH_2)_4^{2+}$, which gives a δ_x of 3.50 for conformation a and 3.73 for conformation b. It is doubtful whether these values can distinguish between the tridentate and bidentate cases, but they certainly do identify the bound peptide-amide ligand as nitrogen.

Since $CuHGL^+$ has the same absorption maximum as $CuHGG^+$, and $CuHLG^+$ differs only slightly, the same calculations and conclusions hold. As noted for the nickel complexes, presence of the isobutyl group α to both coordinating nitrogens increases the ligand-field effect. This is also noted in CuG_2 and CuL_2, where the ν values are 15,900 and 16,000 cm^{-1}, respectively. It is also concluded that coordination of CuL_2 in aqueous solution is the same as in CuG_2 ($2NH_2$, $2COO^-$, and $2H_2O$).

CuH_2GGG^+ in the solid state is known to consist of infinite copper-peptide chains[9] of a "six"-coordinate structure involving the terminal NH_2 and peptide oxygen of one peptide, the COO^- terminal of another peptide, Cl^-, and water. The complex dissolves slowly in water and is assumed to form a six-coordinate species in which waters occupy the nonpeptide-ligand positions. Two questions again arise: namely, is the ligand tridentate or bidentate in solution and is the peptide oxygen or peptide nitrogen bound to the metal? The first question cannot be answered unambiguously. In answer to the second, it seems that the peptide oxygen remains bound, since when δ_{OH_2} or δ_{COO^-} was used to calculate δ_x, values of 3060 and 2930, respectively, were obtained, which are consistent with an oxygen atom coordination.

Acknowledgment. Thanks are due to Mrs. Megan Thompson and Mr. Michael Camp for determining the magnetic data. The work was supported in part by the Research Committee of the Graduate School from funds supplied by the Wisconsin Alumni Research Foundation.

Hexafluoroacetylacetone and Hexafluoroacetic Anhydride

A. L. Andreassen, D. Zebelman, and S. H. Bauer*

Contribution from the Department of Chemistry,
Cornell University, Ithaca, New York 14850. *Received August 8, 1970*

Abstract: The molecular geometries of a pair of isoelectronic molecules have been determined by gas-phase electron diffraction. Hexafluoroacetylacetone, which exists as the enol tautomer, was found to have a planar symmetric ring with the following r_g values: $C_1–C_2 = 1.407 \pm 0.031$ Å, $C_2–C_4 = 1.546 \pm 0.008$ Å, $C–O = 1.259 \pm 0.018$ Å, $C–F = 1.337 \pm 0.007$ Å, $\angle C_2C_1C_3 = 115.2 \pm 2.3°$, $\angle C_1C_2O_2 = 126.4 \pm 1.3°$, $\angle C_1C_3C_5 = 119.7 \pm 1.5°$, $\angle CCF = 110.6 \pm 0.8°$. The enol proton appears to lie in the ring plane. The structure of hexafluoroacetic anhydride is best described as two planar halves which pivot about the central oxygen atom. The r_g values for this compound are $O_1–C_2 = 1.360 \pm 0.019$ Å, $C_2–C_4 = 1.546 \pm 0.010$ Å, $C_1–O_2 = 1.203 \pm 0.010$ Å, $C–F = 1.336 \pm 0.005$ Å, $\angle C_1O_1C_2 = 118.5 \pm 2.6°$, $\angle O_1C_2O_3 = 120.5 \pm 1.9°$, $\angle O_1C_1C_3 = 122.6 \pm 1.1°$, $\angle CCF = 110.2 \pm 0.6°$; the $C_2O_1C_1O_2$ dihedral angle is $20.3 \pm 3.6°$. The above error limits are three times the least-squares-calculated uncertainties for fitting the calculated to the observed $qM(q)$ curves. This has been shown to encompass the estimated experimental errors involved in this study.

The effects of fluorine-for-hydrogen substitution in organic molecules have been the subject of several experimental and theoretical studies.[1–4] The two compounds with which this report is concerned, hexafluoroacetylacetone (HFACT) and hexafluoroacetic anhydride (HFAA), were selected for investigation not only to check whether previously observed trends[1] were followed, but also to determine the structural effects which result from enolization stabilized by intramolecular hydrogen bonding. Indeed, replacement of the central oxygen (O_1) in HFAA with a methylene group leads to significant changes in the central part of the molecule. Also, the structures found for HFACT and HFAA are consistent with published results for related substances.

Experimental Details and Structure Analysis

Both compounds were obtained from Penninsular ChemResearch, Gainesville, Fla. The samples were distilled and their purities checked by infrared and proton nmr analysis. For each substance two sets of convergent-mode diffraction photographs were obtained with the Cornell dual-mode instrument.[5] Patterns were recorded for the region q = 10–55 Å^{-1} at 65 kV with a nozzle-to-plate distance of 253 mm (HVL), and q = 35–122 Å^{-1} at 65 kV with a distance of 124 mm (HVS). All photographs were taken with 4 in. × 5 in. Kodak Electron Image plates. The electron beam wavelength and the sample-to-plate distance were determined from measurements of Debye–Scherer magnesium oxide powder patterns taken concurrently with the gas sample photographs.

The plates were microphotometered on a modified

---

(1) R. L. Hilderbrandt, A. L. Andreassen, and S. H. Bauer, *J. Phys. Chem.*, **74**, 1586 (1970).

(2) M. S. Gordon and J. A. Pople, *J. Chem. Phys.*, **49**, 4643 (1968).

(3) B. Bak, D. Christensen, L. Hansen-Nygard, and J. Rastrup-Andersen, *Spectrochim. Acta*, **13**, 120 (1958).

(4) V. W. Laurie and D. T. Pence, *J. Chem. Phys.*, **38**, 2693 (1963).

(5) S. H. Bauer and K. Kimura, *J. Phys. Soc. Jap.*, **17**, 300 (1962).

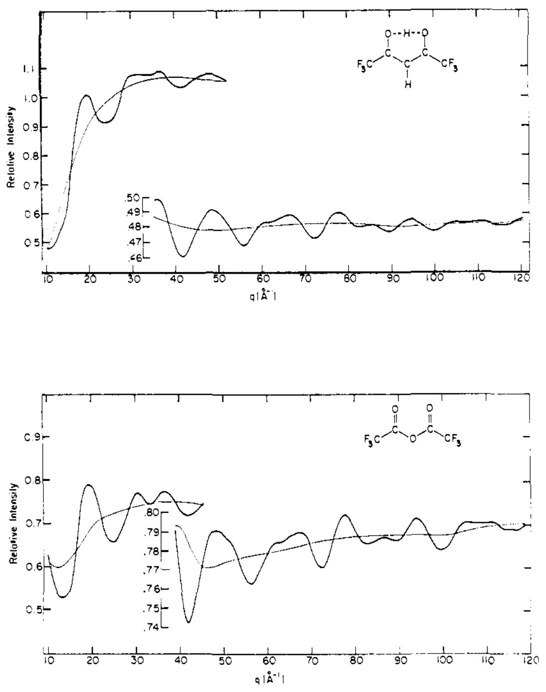

Figure 1. Observed intensities and reduced backgrounds for HFACT and HFAA.

Jarrel–Ash densitometer interfaced with an A-D Data Systems digitizing unit.[6] The HVL plates were scanned and their transmittances were recorded at 200-μ intervals; the HVS plates at 100-μ intervals. These plates were traced several times and the tracings averaged. This procedure reduced the systematic error in finding the center of the tracing and improved the signal-to-noise ratio. The conversion of the recorded transmittances[7,8] to intensities interpolated at unit q [$q = (40/\lambda) \sin(\theta/2)$], and preliminary model testing was carried out on a modified DEC PDP-9 computer. Subsequent analyses were performed with an IBM 360/65 computer. The reduced data and backgrounds for both compounds are plotted in Figure 1. The background was determined through the use of the positivity requirement for the radial distribution curve.[9] The diffraction intensity data have been deposited.[10]

Experimental radial distribution curves and difference curves are plotted in Figure 2. As expected, the curves for HFACT and HFAA show many similarities. The first peak which contains nonbonded distances is centered at 2.17 Å. It is due to the gem fluorine–fluorine (nonbonded) distance, and is the same for both molecules. The peak at 2.2–2.4 Å contains the $O_1\cdots O_2$ and $O_1\cdots O_3$ distances in HFAA and the $C_1\cdots O_1$ and $C_1\cdots O_2$ distances in HFACT. The splitting of this peak for HFACT indicates a fairly large $C_1C_2O_2$ angle. In HFAA this peak permits us to exclude a model in which O_1 points in the same direction as O_2 and O_3.

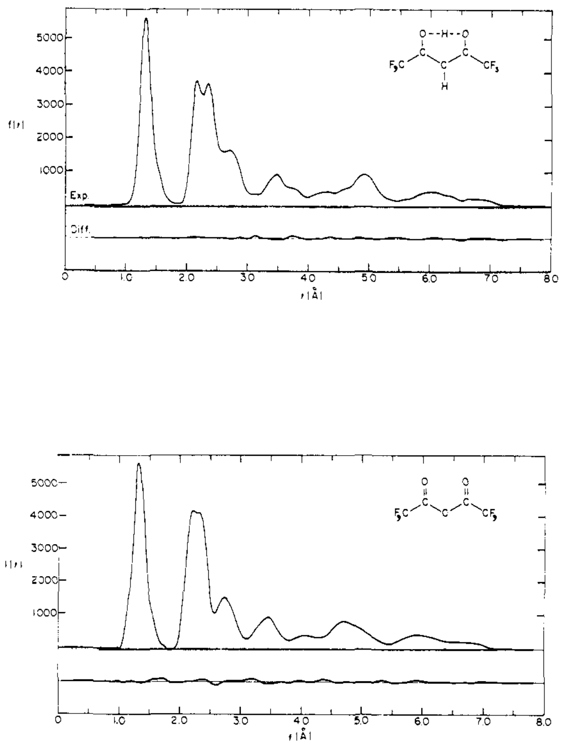

Figure 2. Experimental radial distribution curves and differences between the experimental and theoretical values for the best model for HFACT and HFAA.

The shoulder at 2.7 Å contains the $C_2\cdots O_1$ and $C_3\cdots O_2$ separations in HFACT, and the $C_2\cdots O_2$ and $C_1\cdots O_3$ separations in HFAA. Its location indicates that there is no substantial degree of nonplanarity in either molecule. The well-resolved peak in both curves at 3.55 Å corresponds to the $C_1\cdots F_1$ and $C_1\cdots F_4$ distance in HFACT, and to $O_1\cdots F_1$ and $O_1\cdots F_4$ in HFAA. Freely rotating CF_3 groups would have produced a much broader peak. The mean square amplitudes for this distance (0.090 Å in HFACT and 0.087 Å in HFAA) suggest that rotation of the CF_3 group is hindered by more than 1 kcal. Additional evidence for restricted rotation is found in the peak at 4.9 Å. It corresponds to the contributions from fluorine–oxygen across the ring. Again the peaks are well resolved but somewhat less pronounced in HFAA.

Throughout this study, the elastic and inelastic form factors of Tavard, *et al.*,[11] were used in conjunction with the Bonham-Ukaji phase-shift approximation.[12] The effects of anharmonicity of the molecular vibrations were considered, and an approximate correction[13,14] was introduced. The final parameters and error estimates were obtained from a least-squares fitting of the experimental $qM(q)$ curves. The least-squares program incorporates the following modification suggested by Bonham, *et al.*[15] If Y^i represents the parameter estimates for the ith cycle, and Y^{i-1} the parameters from the preceding cycle, with ΔY^i being the corrections calculated by the Taylor expansion least squares, then

---

(6) S. H. Bauer, R. Jenkins, and R. L. Hilderbrandt, manuscript in preparation.

(7) J. L. Hencher and S. H. Bauer, *J. Amer. Chem. Soc.*, **89**, 5527 (1967).

(8) R. L. Hilderbrandt and S. H. Bauer, *J. Mol. Struct.*, **3**, 325 (1969).

(9) I. L. Karle and J. Karle, *J. Chem. Phys.*, 17, 1052 (1949).

(10) Data will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth St., N. W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit $3.00 for photocopy or $2.00 for microfiche.

(11) C. Tavard, D. Nicholas, and M. Rouault, *J. Chim. Phys. Physicochim. Biol.*, **64**, 540 (1967).

(12) R. A. Bonham and T. Ukaji, *J. Chem. Phys.*, **36**, 72 (1962).

(13) K. Kuchitsu and L. S. Bartell, *ibid.*, **35**, 1945 (1961).

(14) K. Kuchitsu, *Bull. Chem. Soc. Jap.*, **40**, 498 (1967).

(15) T. Strand, D. Kohl, and R. A. Bonham, *J. Chem. Phys.*, **39**, 1306 (1963).

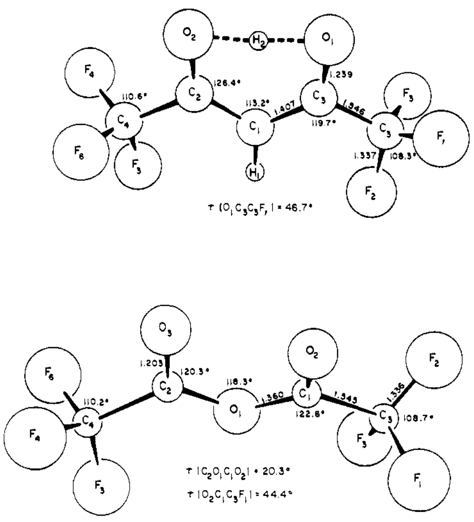

Figure 3. Minimum-energy conformations and least-squares-calculated parameters for HFACT and HFAA.

$$Y^i = Y^{i-1} + \epsilon \Delta Y^i$$

where ϵ is a constant which is allowed to vary between -1.5 and $+1.75$. The convergence rate was thus considerably enhanced. In a particularly favorable case, the number of cycles necessary to achieve convergence with a given set of initial estimates for the parameters was reduced from 11 to 5. A nondiagonal weighting matrix[16] was introduced in this program to take into account the effects of data correlation in the calculation of the least-squares uncertainties. The molecular cartesian coordinates were calculated using Hilderbrandt's method.[17]

The final parameters for both molecules are listed in Table I. The numbering of atoms and schematics of the structures are shown in Figure 3. It is evident that the parameters which characterize corresponding parts of the two molecules agree quantitatively.

Table I. Least-Squares Structure Parameters[a,b]

	HFACT		HFAA
C_1–C_2	1.4065 (0.0102)	O_1–C_1	1.3596 (0.0063)
C_2–C_4	1.5464 (0.0028)	C_2–C_4	1.5455 (0.0043)
C_3–O_1	1.2591 (0.0061)	C_1–O_1	1.2027 (0.0033)
C–F	1.3365 (0.0024)	C–F	1.3358 (0.0018)
C–H	1.0791 (assumed)		
O–H	1.2763 (0.0056)		
$\angle C_2C_1C_3$	115.19 (0.77)	$\angle C_1O_1C_2$	118.50 (0.87)
$\angle C_1C_2O_2$	126.41 (0.44)	$\angle O_1C_2O_3$	120.53 (0.64)
$\angle C_1C_3C_5$	119.71 (0.49)	$\angle O_1C_1C_3$	122.58 (0.36)
$\angle$CCF	110.65 (0.25)	$\angle$CCF	110.23 (0.19)
$\angle$FCF	108.27 (0.71)	$\angle$FCF	108.71 (0.20)
$\angle O_2H_2O_1$	175.51 (3.85)		
l_{C-F}	0.0437 (0.0032)	l_{C-F}	0.0578 (0.0014)
$l_{C_1-C_2}$	0.0525 (0.0126)	$l_{C_2-C_4}$	0.0437 (0.0112)
$l_{C_2-C_4}$	0.0521 (0.0051)	$l_{C-O_{av}}$	0.0433 (0.0057)
$l_{C_8-O_1}$	0.0508 (0.0068)		
σ	0.02080	σ	0.02437

[a] The calculated least-squares uncertainties are given in parentheses. The error limits quoted in the text are three times these values. The factor of 3 has been shown to be large enough to encompass all other uncertainties.[8] [b] Bond lengths in ångströms, angles in degrees.

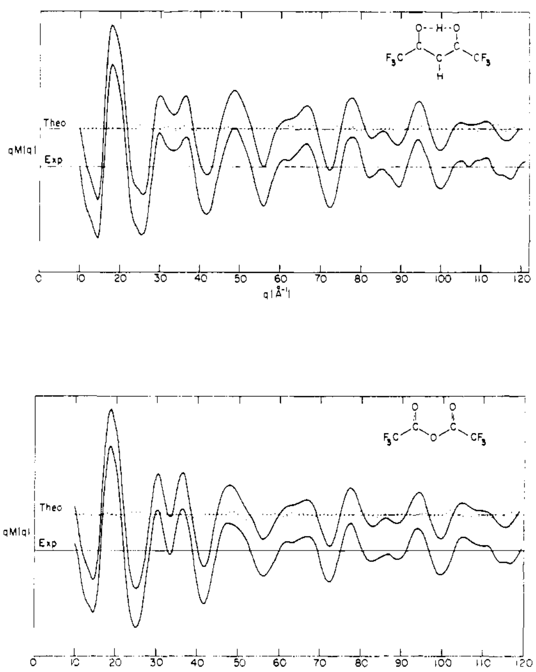

Figure 4. Experimental and theoretical $qM(q)$ curves; the dots show the differences between the calculated and experimental curves for HFACT and HFAA.

Proton nmr studies of β-dicarbonyls in the pure liquid phase[18] indicate that replacement of the methyl groups of acetylacetone by the strongly electronegative perfluoromethyl groups shifts the keto–enol equilibrium from 81 to 100% enol.[19] In the gas phase[20–22] and in fairly nonpolar solvents[23] the enol tautomer is further stabilized by elimination of intermolecular hydrogen bonding. In the structure analysis the ring in HFACT was not constrained to a plane; however, the least-squares calculation converged to a $C_2C_1C_3O_1$ dihedral angle of 6.0 ± 5.1°. This small deviation from coplanarity may be attributed to thermal "shrinkage."[24] A model for which there were two different ring carbon–carbon distances and two carbon–oxygen distances was considered. However, this model failed to converge. For both molecules there were no particularly strong parameter correlations, with the exception of the C–F distance and the CCF angle in HFACT, which exhibited a correlation of +0.96. However, the values deduced agree well with the averages listed in Table II (see below).

C_{3v} symmetry was imposed on the CF_3 groups in both molecules, assuming the pyramid axes coincide with the extension of the C–C bond. Since a rigid-rotor model was indicated by the experimental radial distribution curve, the conformational angle of the CF_3 groups was inserted as a parameter. In HFACT a least-squares minimum was obtained with the $O_1C_3C_5F_1$ dihedral angle at 46.7 ± 2.0°. In this model, the CF_3 groups are

---

(16) Y. Murata and Y. Morino, *Acta Crystallogr.*, 20, 605 (1966).

(17) R. L. Hilderbrandt, *J. Chem. Phys.*, **51**, 1654 (1969).

(18) J. L. Burdett and M. T. Rogers, *J. Amer. Chem. Soc.*, **86**, 2105 (1964).

(19) R. L. Lintvedt and H. F. Holtzclaw, Jr., *ibid.*, **88**, 2713 (1966).

(20) J. B. Conant and A. F. Thompson, Jr., *ibid.*, **54**, 4039 (1932).

(21) R. Schreck, *ibid.*, 71, 1881 (1949).

(22) E. Funke and R. Mecke, "Hydrogen Bonding," D. Hadzi, Ed., Pergamon Press, London, 1959.

(23) J. Powling and H. J. Bernstein, *J. Amer. Chem. Soc.*, **73**, 4353 (1951).

(24) S. J. Cyvin, "Molecular Vibrations and Mean Square Amplitudes," Elsevier, Amsterdam, 1968.

Table II[a]

Compound	CF$_3$		=CF$_2$		≡CF	
	(C–F)	∠FCF	(C–F)	∠FCF	(C–F)	Ref
$F_3C—CF_3$	1.320	109.5				*b*
$F_3C—CH_3$	1.344	107.3				*c*
$F_3C—CN$	1.335	107.5				*d*
F_3COCH_8	1.339	108.7				*e*
$(F_3C)_2C═CH_2$	1.327	108.5				*f*
$(F_3C)_2C═NH$	1.324	109.0				*f*
$(F_3C)_2C═O$	1.335	108.7				*f*
$F_3CC≡CCF_3$	1.333	108.3				*g*
HFAA	1.336	108.7				*h*
HFACT	1.337	108.3				*h*
$F_2C═CH_2$			1.323	109.1		*i, m*
$F_2C═CFH$			1.340	108.6		*m*
$F_2C═CF_2$			1.313	114.0		*j*
$F_2C═O$			1.312	108.0		*k*
$F_2C═CF—CF═CF_2$			1.323	111.0		*g*
FC≡CH					1.279	*l*
FC≡N					1.262	*l*
Av	1.333	108.5	1.322	110.1	1.271	

[a] Bond lengths in ångströms, angles in degrees. [b] D. A. Swick and I. L. Karle, *J. Chem. Phys.*, **23**, 1499 (1955). [c] R. Schwendeman, Thesis, University of Michigan, 1956. [d] L. F. Thomas, J. S. Heeks, and J. Sheridan, *Z. Electrochem.*, **61**, 935 (1957). [e] A. L. Andreassen and S. H. Bauer, manuscript in preparation. [f] R. L. Hildebrandt, A. L. Andreassen, and S. H. Bauer, *J. Phys. Chem.*, **74**, 1586 (1970). [g] C. H. Chang, A. L. Andreassen, and S. H. Bauer, manuscript in preparation. [h] This work. [i] V. W. Laurie and D. T. Pence, *J. Chem. Phys.*, **38**, 2693 (1963). [j] I. L. Karle and J. Karle, *ibid.*, **18**, 963 (1950). [k] V. W. Laurie and D. T. Pence, *ibid.*, **37**, 2995 (1962). [l] J. K. Tyler and J. Sheridan, *Trans. Faraday Soc.*, **59**, 2661 (1963). [m] J. Carlos, Cornell University, unpublished.

rotated in opposite directions by an equal amount. The HFAA model which best agrees with the experimental data consists of two planes connected through the central oxygen. The dihedral angle between the two planes was found to be 20.3 ± 3.5°. The angular rotation of the CF$_3$ groups was also introduced as a parameter, which in the least-squares calculation converged to 44.4 ± 2.4°, in good agreement with the value obtained for HFACT. These are "average structure" values.

The experimental $qM(q)$ curves are plotted in Figure 4. As would be expected, there are only small differences in the positioning of the maxima and minima due to the small difference in ring dimensions.

Discussion

The magnitudes of the structural parameters determined in this study are consistent with those reported for molecules with similar features. In highly fluorinated carbon compounds the observed C—F distances and FCF angles fall into three categories, characteristic of F_3C–, F_2C═, and FC≡, as summarized in Table II. It has been shown[1] that replacement of a CH$_3$ group by a CF$_3$ group leads to a long C–CF$_3$ distance compared with ethane (1.5319 Å).[25] The values of 1.545 and 1.546 Å found in this study are in good agreement with those in 1,1,1-trifluoroacetaldehyde (1.540 Å),[26] hexafluoroacetone (1.549 Å),[1] and hexafluoroacetonimine (1.549 Å).[1] The C—O distance in HFACT (1.259 ± 0.018 Å) is considerably longer than the C═O bond length in acetone (1.210 Å;[1] 1.215 Å[27]) and in 1,1,1-trifluoroacetone (1.207 Å).[28] However, it is considerably shorter than the C–O distance in dimethyl ether (1.410 Å),[29] perfluorodimethyl peroxide (1.398 Å),[30] methanol (1.428 Å),[31] and in HFAA. The C$_1$–C$_2$ distance in HFACT is considerably shorter than that observed for single bonds (1.46–1.56 Å) but longer than those reported for double bonds (1.31–1.34 Å). It is almost equal to the C–C distance in benzene (1.397 Å).[32] These values argue strongly for extensive electron delocalization in the enol ring.

An "average" structure for metal chelates of acetylacetone has been proposed by Lingafelter and Braun.[33] The ring distances in HFACT and this average structure agree to within the experimental uncertainties. The C–C distance in HFACT (1.407 ± 0.031 Å) is slightly longer than the corresponding distance in the chelate (1.390 Å). However, the C–O distance is slightly shorter (1.259 ± 0.018 Å in HFACT; 1.274 Å for the chelate). This is consonant with recent normal-coordinate analyses of acetylacetone and HFACT.[34] The $C_1C_2O_2$ angle (126.4 ± 1.3°) in HFACT agrees well with the average (125.3°), as does the $C_1C_3C_5$ angle (119.7 ± 1.5° in HFACT; 119.85° for the chelate). The only discrepancy noted is in the $C_2C_1C_3$ angle (115.2 ± 2.3° in HFACT). The large value (124.02°) found for the average chelate structure may be attributed to the larger bonding radius of the chelated metal atom which forces the ring to expand.

Convergence of the least-squares calculation is not sensitive to the position of the enol proton. The $O_1\cdots O_2$ nonbonded distance in HFACT (2.551 ± 0.033 Å) is comparable to that in several compounds in which the proton is symmetrically placed between the two oxygens. For example, in KH maleate this distance is 2.44 Å;[35] in KH bisphenyl acetate, 2.54 Å;[36] and in chromous acid, 2.49 Å.[37] Both diffraction and spectroscopic data indicate that with an O···O distance of approximately 2.5 Å, the O–H distance is long, and

---

(25) K. Kuchitsu, *J. Chem. Phys.*, **49**, 4456 (1968).

(26) R. Schwendeman, Thesis University of Michigan, 1956.

(27) J. Swalen and C. C. Costain, *J. Chem. Phys.*, 31, 1562 (1959).

(28) A. L. Andreassen and S. H. Bauer, manuscript in preparation.

(29) U. Blukis, B. H. Kasai, and J. Myers, *J. Chem. Phys.*, **38**, 2753 (1963).

(30) R. L. Hilderbrandt and S. H. Bauer, manuscript in preparation.

(31) K. Kimura and M. Kubo, *J. Chem. Phys.*, **30**, 151 (1959).

(32) A. Langseth and B. P. Stoicheff, *Can. J. Phys.*, **34**, 350 (1956).

(33) E. C. Lingafelter and R. L. Braun, *J. Amer. Chem. Soc.*, **88**, 2951 (1966).

(34) H. Ogoshi and K. Nakamoto, *J. Chem. Phys.*, **45**, 3113 (1966).

(35) S. W. Peterson and H. A. Levy, *ibid.*, **29**, 948 (1958).

(36) G. E. Bacon and N. A. Curry, *Acta Crystallogr.*, 13, 717 (1960).

(37) W. C. Hamilton and J. A. Ibers, *ibid.*, **16**, 1209 (1963).

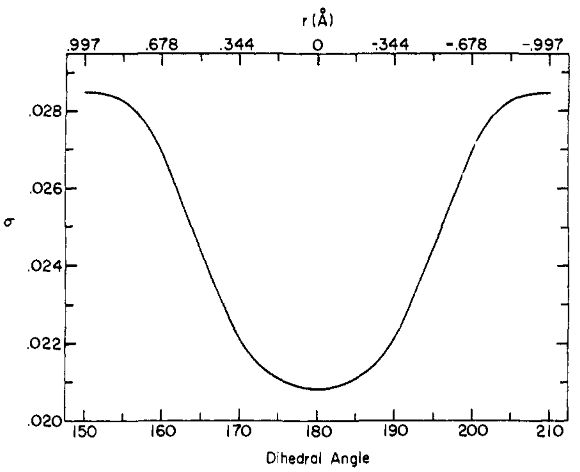

Figure 5. Total standard deviation in the $qM(q)$ function *vs.* the $C_5C_3O_1H_2$ dihedral angle (bottom scale, 180° is planar). The vertical distance of the proton (H_2) above and below ring plane is given at the top scale for HFACT.

as the O···O separation increases (to 2.75–2.95 Å), the proton assumes an unsymmetrical location at approximately 1.0 Å from one of the oxygen atoms.[38] In this investigation the converged location of the proton, assuming it was symmetrically placed and in the plane, was approximately collinear with the two oxygen atoms ($\angle O_1H_2O_2$ = 175.5 ± 11.6°). The parameter most conveniently refined was the $C_1 \cdots H_2$ nonbonded distance, 1.960 ± 0.118 Å. Attempts at refining other positional parameters for the enol proton failed to converge. Since it has been observed that in metal complexes the ring exhibits a fold, that is the metal atom is not in the plane of the ring,[39] a least-squares program was run in which the proton was constrained to multiples of 5° out of plane, but symmetrically disposed. As can be seen from Figure 5, the lowest standard deviation was obtained with H_2 at 180°, *i.e.*, in the plane.

The conclusion that HFAA possesses C_2 symmetry confirms recent ir work on acetic anhydride.[40] The electron diffraction data support the C_2 conformation wherein the C=O bonds of the acetyl groups point almost in the same direction; the net difference of 20° is due to a small rotation of these groups about the C—O$_1$ bonds out of the planar conformation, in opposite directions. DeKok and Romers,[41] in their paper on monochloroacetic anhydride, conclude that the molecule has C_1 symmetry in the crystal. This was attributed to crystal packing forces. They suggested that in the gas phase the molecule would possess the higher C_2 symmetry. The dihedral angle between the two acetyl planes was found to be 43° in the crystal. This corresponds to the angle found for HFAA (20.3 ± 3.6°) in the gas phase.

Acknowledgments. This work was supported by the National Science Foundation under Grant No. GP-7794. The DEC PDP-9 computer is supported under Grant No. GP-8652.

(38) R. D. Ellison and H. A. Levy, *Acta Crystallogr.*, **19**, 260 (1965).

(39) J. V. Silverton and J. L. Hoard, *Inorg. Chem.*, **2**, 243 (1963).

(40) P. Mirone, B. Fortunato, and P. Canziani, *J. Mol. Struct.*, **5**, 283 (1970).

(41) A. J. DeKok and C. Romers, *Recl. Trav. Chim. Pays-Bas*, **88**, 625 (1969).