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Structure and Conformation of Perfluoromethyloxalate, $CF_3OC(O)-C(O)OCF_3$, in the Crystal and in the Gas Phase

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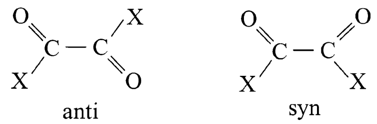
The geometric structure and conformational properties of perfluoromethyloxalate, $CF_3OC(O)-C(O)OCF_3$, have been studied in the gas phase by gas electron diffraction (GED) and in the solid state by X-ray crystallography. The experimental investigations were supplemented by quantum chemical calculations using the MP2 and B3LYP methods with 6-31G* and 6-31++G(2df) basis sets, respectively. The GED analysis results for the gaseous state in a mixture of two planar conformers with both C═O bonds antiperiplanar (ap) to each other (C_{2h} symmetry) or both C═O bonds synperiplanar (sp) to each other (C_{2v} symmetry). The ratio ap:sp of 58(12)%:42(12)% corresponds to $\Delta G^0 = 0.19(37)$ kcal/mol. This value is reproduced satisfactorily by the quantum chemical calculations: 0.42 kcal/mol (MP2) and 0.67 kcal/mol (B3LYP). The presence of a mixture of two conformers with nearly equal contributions is confirmed by the IR(gas) spectrum. In the solid state, four independent molecules with ap conformation (C_i symmetry) occur in the unit cell.

Introduction

Geometric structures and conformational properties of dicarbonyl compounds of the type XC(O)−C(O)X have attracted great interest for several decades by many experimentalists and theoreticians. Two conformations are feasible, anti and syn (Scheme 1) where anti implies antiperiplanar (ap) or anticlinal (ac) and syn implies synperiplanar (sp) or synclinal (sc). The kind of conformations and their relative stabilities depend strongly on the substituent X. In the parent compound ethylene glycol, HC(O)−C(O)H, two stable planar conformers, a low-energy ap and a high-energy sp form, exist in the gas phase. Their structures have been determined by gas electron diffraction (GED) and microwave spectroscopy (MW), respectively.[1,2] Experimental values for the enthalpy difference $\Delta H° = H°(\mathrm{sp}) - H°(\mathrm{ap})$ vary between 3.22 and 4.83 kcal/mol.[3] The most recent value is $\Delta H° = 4.45(14)$ kcal/mol.[4] Various quantum chemical calculations predict $\Delta H°$ values ranging from 3.0 to 6.0 kcal/mol.[5] In the crystal, ethylene glycol exists in the sc (gauche) conformation, networked by intermolecular OH···O hydrogen bonds.[6] In a GED analysis for dimethylglyoxal, $CH_3C(O)-C(O)CH_3$, only a single ap conformer was observed, even at temperatures as high as 525 °C.[7] Vibrational spectra of gaseous and liquid oxalyl fluoride, FC(O)−C(O)F, have been interpreted in terms of a mixture of two planar conformers.[8−10] The planarity of the sp form has been demonstrated by microwave spectroscopy.[11] $\Delta H°$ values between 0.38(7) and 1.05 kcal/mol have been reported. This result is reproduced by ab initio calculations, which predict an energy difference between 0.43 and 0.97 kcal/mol.[9,12] From spectroscopic data[13] and GED analyses[14] of oxalyl chloride it was concluded that this molecule exists as a mixture of two conformers, a low-energy ap form and a sc (gauche) conformer with higher energy. According to the GED experiment the dihedral angle ϕ(O═C−C═O) of the sc form is 74(39)° and the enthalpy difference $\Delta H° = 0.75(50)$ kcal/mol. A discrepancy exists about quantum chemical calculations. All potential functions for internal rotation around the C−C bond, which were calculated by Danielson et al. in the context of the GED experiment using HF and MP2 approximations with different basis sets, possess only a single minimum at $\phi = 180°$ (ap conformer), except for the function derived with the highest level, MP2/TZ2P.[14] This potential function possesses an additional shallow minimum, corresponding to a sc structure with ϕ near 90°. On the other hand, Durig et al.[13] report an "estimated" potential function derived with the HF/6-31G* method, which possesses a second minimum at $\phi = 39°$ and the authors claim to obtain minima at 66° with all other computational methods. However, none of these results could be reproduced and thus are questionable.

SCHEME 1



A GED study of oxalic acid, HOC(O)−C(O)OH, results in an ap structure with two intramolecular hydrogen bonds.[15] A second conformer with an ap structure and a single hydrogen bond and ca. 1.7 kcal/mol higher in energy was observed by IR(matrix) spectroscopy.[16] Quantum chemical calculations predict a total of six stable conformations for this compound with relative energies up to 15 kcal/mol.[17] Crystalline dimethyl-

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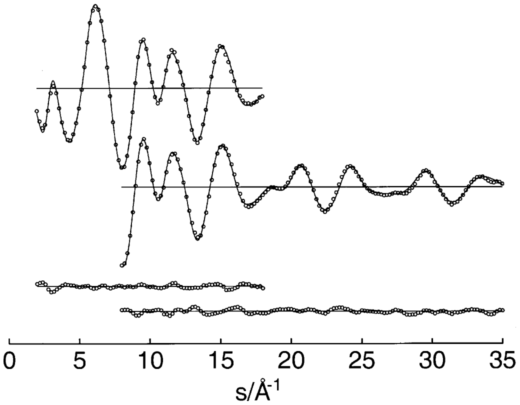

Figure 1. Experimental molecular scattering intensities for long (above) and short (below) nozzle-to-plate distances and residuals.

oxalate, $CH_3OC(O)—C(O)OCH_3$, possesses an ap structure with the O—CH_3 bonds eclipsing the adjacent C=O bonds (C_{2h} symmetry).[18] Controversial interpretations of vibrational spectra of the liquid and gaseous phases have been proposed: (1) mixture of two conformers,[19,20] (2) single nonplanar conformer with C_2 symmetry, in which the two $CH_3OC(O)$ groups are rotated relative to each other around the C—C bond,[21] or (3) single conformer with planar C_2O_4 skeleton and the methyl groups rotated out of the carbonyl planes.[22] A GED study that is presently being performed in combination with quantum chemical calculations at the University of Moscow is expected to resolve this discrepancy.

Thus, conformational properties of dicarbonyl compounds of the type XC(O)—C(O)X depend on the substituent X and in some cases different experimental and theoretical methods may lead to different results. Additional studies are desirable to obtain deeper insight into the bonding properties of such compounds. In the present publication we report a structural and conformational study of perfluoromethyl oxalate (PFMO), based on a GED experiment and on quantum chemical calculations as well as on a crystal structure analysis. The synthesis of this compound was reported by Varetti and Aymonino.[23] From vibrational spectra it was concluded that this compound exists in the solid state as a single conformer with ap structure (C_{2h} symmetry) and as a mixture of a planar ap and a nonplanar conformer in the liquid and gaseous states.[24]

Experimental Section

$CF_3OC(O)—C(O)OCF_3$ was synthesized by the photochemical reaction of CF_3OOCF_3 with CO.[23,24] Fractionation of the reaction products through traps at −60, −120, and −196 °C yields pure PFMO, which is retained as a colorless liquid in the −60 °C trap. The final purity (>98%) of the compounds was checked by IR ^{13}C NMR and ^{19}F NMR spectroscopy.

Electron diffraction intensities were recorded with a Gasdiffraktograph KD-G2[25] at 25 and 50 cm nozzle-to-plate distances and with an accelerating voltage of about 60 kV. The sample was cooled to −5 °C and the inlet system and nozzle were at room temperature. The photographic plates were analyzed with the usual methods[26] and averaged molecular intensities in the s-ranges 2−18 and 8−35 Å^{-1} ($s = (4\pi/\lambda) \sin \vartheta/2$, λ = electron wavelength, J = scattering angle) are shown in Figure 1.

Quantum Chemical Calculations

Based on earlier results for trifluoromethyl fluoroformate, $CF_3OC(O)F$, and perfluorodimethyl carbonate, $(CF_3O)_2CO$, in which the CF_3 groups prefer synperiplanar orientation relative to the C=O bonds,[27] structure optimizations for PFMO were started with such orientation of both CF_3 groups. The geometry was optimized for different fixed dihedral angles ϕ(O=C—C=O) from 0° to 180° using MP2 approximation with 6-31G* basis sets and the hybrid method B3LYP with 6-31++G(2df) basis sets. Both methods predict two stable conformers with planar skeletons and $\phi = 180°$ (anti, C_{2h} symmetry) and $\phi = 0°$ (syn, C_{2v} symmetry). The potential curves for internal rotation around the C—C bond, which were derived with both methods, are shown in Figure 2 together with the curve derived from the GED experiment (see below). The shape of the calculated potential functions depends rather strongly on the computational method. The energy difference between syn and anti forms is predicted to be $\Delta E = 0.48$ kcal/mol by the MP2 approximation and the barrier to internal rotation near 90° to be 1.73 kcal/mol. The B3LYP method predicts $\Delta E = 0.73$ kcal/mol and a barrier of 1.10 kcal/mol. The differences between the Gibbs free energies, $\Delta G°$, are very close to the energy differences and are listed in Table 1. Vibrational frequencies were calculated with the B3LYP/6-31G* method. A very low frequency for the torsion around the C—C bond of 18 cm^{-1} is predicted for both

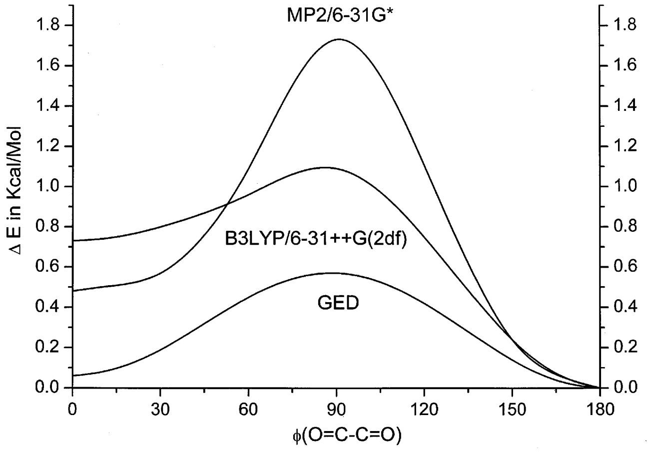

Figure 2. Calculated and experimental potential function for internal rotation around the C—C bond.

TABLE 1: Experimental and Calculated Geometric Parameters (Å and deg) and Conformational Composition of Perfluoromethyloxalate

	GED[a]			X-ray[b]	MP2[c]	B3LY[d]
	ap	sp		ap	ap	ap
C2—C2′	1.515(17)	1.517(17)	p1	1.551(3)	1.532	1.544
C2=O2	1.185(6)	1.185(6)	p2	1.190(1)	1.206	1.189
C2—O1	1.355(8)	1.355(8)	p3	1.370(1)	1.371	1.364
O1—C1	1.379(8)	1.379(8)	p3	1.396(1)	1.392	1.389
$(C—F)_{mean}$	1.318(4)	1.318(4)	p4	1.322(1)	1.332	1.327
C2—C2′=O2′	124.1(16)	120.8(16)	p5	125.3(2)	125.6	125.3
C2—C2′—O1′	109.6(13)	113.1(13)	p6	108.0(2)	107.6	107.9
C1—O1—C2	118.2(8)	118.2(8)	p7	117.9(1)	116.9	119.2
F—C—F	109.0(6)	109.0(6)	p8	108.9(1)	109.3	109.3
tilt (CF_3)[e]	3.5[f]	3.5[f]		3.1(1)	3.5	3.5
contribution %	58(12)[g]	42(12)[g]		100	66	75
$\Delta G°$ (kcal/mol)[f]	0.19(37)[g]				0.42	0.67
V_2 (kcal/mol)	0.06(28)[h]				0.48	0.73
V_4 (kcal/mol)	0.54(39)[h]				1.49	0.74

[a] r_a values with 3σ uncertainties. For atom numbering see Figure 4. [b] Mean values of four molecules, uncertainties are σ values. [c] 6-31G* basis sets. [d] 6-31++G(2df) basis sets. [e] Tilt angle between C_3 axis of CF_3 group and O—C bond direction, toward oxygen lone pairs. [f] Not refined. [g] From least-squares analysis with two rigid conformers. [h] From least-squares analysis with dynamical model.

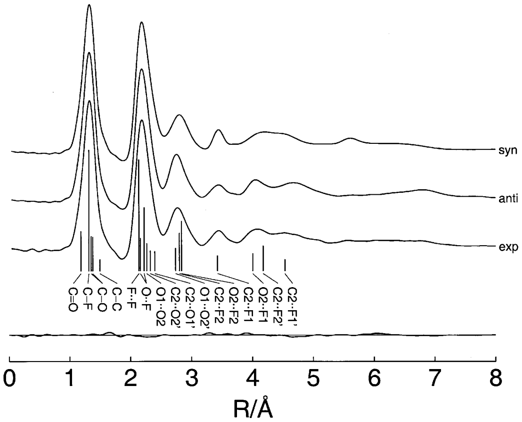

Figure 3. Experimental and calculated radial distribution functions and difference curve for mixture.

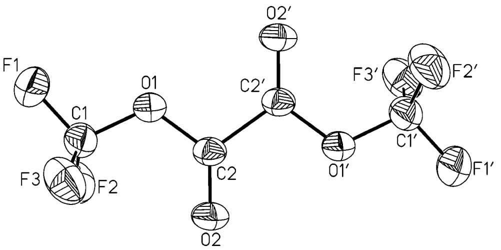

Figure 4. Numbering scheme and presentation of one of the four independent crystallographically centrosymmetric molecules (50% thermal ellipsoid plot) of $CF_3OC(O)-C(O)OCF_3$.

conformers. Cartesian force constants were transformed to symmetry constants that were used for calculating vibrational amplitudes with the program ASYM40.[28] The search of the conformational space with the B3LYP method resulted in a third stable conformer, in which both CF_3 groups are antiperiplanar with respect to the C═O bonds and the two $CF_3OC(O)$ groups are rotated relative to each other by $\phi(O{=}C{-}C{=}O) = 109.1°$. The energy of this conformer is 8.4 kcal/mol higher than that of the ground-state structure and therefore it is not considered in the further analysis. All quantum chemical calculations were performed with the GAUSSIAN98 program package.[29]

Gas-Phase Structure Analysis

The experimental radial distribution function (RDF) derived by Fourier transformation of the molecular scattering intensities, is shown in Figure 3, together with the calculated RDFs for anti and syn conformers. An artificial damping function $\exp(-\gamma s^2)$ with $\gamma = 0.0019$ Å^2 was used. A preliminary analysis of the experimental RDF indicated that it can be reproduced satisfactorily only with a mixture of two conformers in a ratio of about 1:1 and nonplanar structures that are twisted around the C—C bond. In the next step a model consisting of two "rigid" conformers was used. The following constraints were applied in the least-squares fitting of the molecular intensities. (1) C_2 overall symmetry and local C_{3v} symmetry for the CF_3 groups with a tilt angle between the C_3 axis and the O—C bond direction and staggered orientation. According to quantum chemical calculations the C—F bond lengths deviate by less than 0.003 Å and F—C—F angles by less than 0.1° from the respective mean values. (2) The difference between the two C—O single bonds, $\Delta CO = (C1{-}O1) - (O1{-}C2)$ (see Figure 4 for atom numbering), and the tilt angle of the CF_3 groups were set to calculated (MP2) values. (3) The changes of the C—C═O and C—C—O angles between anti and syn conformers were constrained to the calculated differences. Both methods predict equal differences for these two angles of −3.3° for C—C═O and +3.5° for C—C—O, respectively. All bond lengths and remaining bond angles were set equal in both conformers. Calculations predict differences of less than 0.002 Å and 0.1°, respectively. (4) Only six vibrational amplitudes for distances, which do not depend on the torsion around the C—C bond, were included in the refinement. All other amplitudes were set to the calculated values, which included the contributions from the low-frequency torsional vibration. With these assumptions four bond lengths, four bond angles, the dihedral angles ϕ for both conformers, six vibrational amplitudes and the relative ratio of both conformers were refined simultaneously. This least squares refinement resulted in a mixture of 58(12)% anti conformer with $\phi = 144(5)°$ and 42(12)% syn conformers with $\phi = 26(8)°$. These effective dihedral angles can be interpreted either in terms of two nonplanar equilibrium structures with small amplitude torsional vibrations or in terms of two planar equilibrium structures with a large-amplitude torsional motion around the C—C bond. The agreement factor for the molecular intensities from the long nozzle-to-plate distance, which are more sensitive toward conformational properties, is $R_{50} = 4.95\%$.

In the next step a dynamic model consisting of 13 pseudoconformers with ϕ between 0° and 180° in steps of 15° was used. Variations of the C2—C2′ bond length and the C2—C2′═O2′ and C2—C2′—O1′ angles, which occur during internal rotation, were set to the calculated values. The C2—C2′ bond shortens by 0.013 Å between the planar and perpendicular conformation. Vibrational amplitudes for each pseudoconformer were derived from symmetry force constants and contributions of the torsional vibration around the C—C bond were excluded. The pseudoconformers were weighted with a Boltzmann factor using a potential function of the type $V = V_2/2(1 + \cos \phi) + V_4/2(1 - \cos 2\phi)$. V_2 corresponds to the energy difference between syn and anti conformers, and the barrier to internal rotation near 90° is given by $V_4 + V_2/2$. The potential functions obtained with the quantum chemical methods (Figure 1) are reproduced well with such an expression. In the least-squares analysis four bond lengths, four bond angles, six vibrational amplitudes ($l1$ to $l6$) and the potential constants V_2 and V_4 were refined. The following correlation coefficients had values larger than |0.7|: $p3/p4 = -0.86$, $p4/p8 = 0.82$, $p3/l1 = -0.84$ and $p4/l1 = 0.74$. The results of this refinement are summarized in Table 1 together with the calculated values. The potential function derived from the GED analysis is shown in Figure 2. Bond lengths and bond angles of this analysis agree with those obtained with the rigid model within their standard deviations σ. The uncertainties given in Tables 1 and 2 are 3σ values. The agreement factor of the analysis with a dynamic model, $R_{50} = 4.77\%$, is slightly lower than that for the rigid model.

Additional least squares refinements were performed with potential functions, which possess a small Gaussian-shaped hump at $\phi = 0°$ and 180° and thus simulate nonplanar equilibrium structures of the anti and syn conformers. The fit of the experimental intensities did not improve for low humps and the agreement factor increased for humps larger than 0.1 kcal/mol. Thus, we conclude from the GED analysis that both conformers possess planar or nearly planar equilibrium structures.

X-ray Structure Determination

The reflection intensities of a colorless single crystal of $C_4F_6O_4$ (226.04 Da) with the approximate size 0.26 × 0.23 × 0.18 mm was measured on a Siemens SMART CCD diffractometer (Mo Kα radiation) at 173(2) K, which resulted in cell

TABLE 2: Experimental and Calculated (B3LYP/6-31G*) Vibrational Amplitudes for the a*p* Conformer[a]

	GED[b]		B3LYP		GED[b]		B3LYP
C2═O2	0.037[c]		0.037	O1···O1′	0.068(21)	*l*4	0.062
C2—O1	0.046[c]		0.046	O2···F1	0.093(19)	*l*5	0.085
C1—O1	0.048[c]		0.048	O2···C1′	0.102[c]		0.102
C1—F	0.044(4)	*l*1	0.044	C2′···F2	0.136[c]		0.136
C2—C2′	0.051[c]		0.051	C2′···F1	0.093(19)	*l*5	0.085
F1···F2	0.058(4)	*l*2	0.056	O2′···F1	0.140[c]		0.140
O1···F1	0.059[c]		0.059	O1···C1′	0.074[c]		0.074
C1···O1′	0.063[c]		0.063	O2′···F2	0.198(42)	*l*6	0.196
O2···O1	0.051[c]		0.051	O1′···F2	0.198(42)	*l*6	0.202
C1···C2	0.062[c]		0.062	O1′···F1	0.075[c]		0.075
C2···O2′	0.060[c]		0.060	C1···C1′	0.075[c]		0.075
O1′···O2	0.094[c]		0.094	C1′···F2	0.198(42)	*l*6	0.207
O2···C1	0.092[c]		0.092	F2···F2′	0.329[c]		0.329
C2···F2	0.113(14)	*l*3	0.116	C1′···F1	0.095[c]		0.095
O2···F2	0.181[c]		0.181	F2···F3′	0.166[c]		0.166
O2···O2′	0.058[c]		0.058	F1···F2′	0.279[c]		0.279
C2···F1	0.068(21)	*l*4	0.061	F1···F1′	0.086[c]		0.086

[a] Experimental values derived from the rigid two-conformer model. For atom numbering, see Figure 4. [b] Uncertainties are 3σ values. [c] Not refined.

dimensions $a = 8.819(2)$ Å, $b = 9.109(2)$ Å, $c = 10.148(3)$ Å, $\alpha = 103.536(4)°$, $\beta = 107.370(4)°$, $\gamma = 90.053(4)°$, $V = 754.1(3)$ Å^3, triclinic, space group $P\bar{1}$, Z = 4, ρ(calc) = 1.991 g cm^{-3}, θ(min/max.) = 2.17−28.39°, full sphere data collection in ω at 0.3° scan width, two runs with 720 frames ($\phi = 0°, 270°$) and two runs with 436 frames ($\phi = 88°, 180°$), index ranges $-11 \leq h \leq 11$, $-12 \leq k \leq 12$, $-13 \leq l \leq 13$, data reduction with Bruker AXS SAINT program Vers. 6.02A, empirical absorption correction Bruker AXS SADABS program multiscan V2.03, max./min transmission 1.00/0.58, *R*(merg) before/after correction 0.110/0.0459, structure solution by direct methods and refinement on F^2 with Bruker AXS SHELXTL Vers. 5.10 DOS/WIN95/NT, 9011 reflections collected, 3711 independent [*R*(int) = 0.0286], data/restraints/parameters: 2935/0/253, goodness-of-fit on F^2 1.066, weighting details $w = 1/[\sigma^2(F_o^2) + (0.0962P)^2 + 0.099P]$, where $P = (F_o^2 + 2F_c^2)/3$, final *R* indices [$I > 2\sigma(I)$] $R1 = 0.0546$, $wR2 = 0.1417$, *R* indices (all data) $R1 = 0.0649$, $wR2 = 0.1548$, largest difference peak and hole: +0.426 and −0.432 e Å^{-3}. Complementary crystallographic data have been deposited at the Cambridge Crystallographic Data Centre (deposition number CCDC 219229).

Discussion

The GED intensities are reproduced almost equally well with a rigid model consisting of a mixture of nonplanar anti and syn conformers and with a dynamic model with two planar ap and sp conformers and equal contributions. Planar equilibrium structures of both conformers are also predicted by quantum chemical calculations (MP2 and B3LYP). The GED analysis results in a barrier to internal rotation around the C—C bond, 0.57(48) kcal/mol, lower than those predicted by quantum chemical calculations, 1.73 kcal/mol (MP2) and 1.10 kcal/mol (B3LYP). In the IR(gas) spectra two bands are observed in the region of the C═O vibrations at 1823 (vs) and 1842 cm^{-1} (s). For a mixture of ap and sp conformers three C═O vibrations are expected, ν_{as} for the ap form with C_i symmetry and ν_s and ν_{as} for the sp form. The B3LYP method predicts ν_{as} =1882 cm^{-1} (vs) for the ap conformer and ν_s = 1893 cm^{-1} (s) for the sp conformer. ν_{as} for the sp form is predicted to occur at 1881 cm^{-1}, with less than one-tenth of the intensity of the antisymmetric vibration. This vibration coincides with ν_{as} for the ap conformer. The calculated splitting of the two strong bands, $\Delta\nu = 11$ cm^{-1}, is smaller than the observed splitting of 19 cm^{-1}, but the IR(gas) spectrum confirms the presence of two planar conformers with similar contributions.

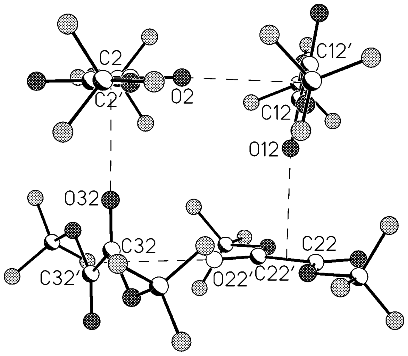

Figure 5. Presentation of the mutual arrangement of the four independent molecules and molecules with closest intermolecular contacts (carbonyl O···(center of molecule)) indicated as dashed lines.

In the solid state, four independent and crystallographically centrosymmetric molecules (C_i symmetry, ap conformation) are found in the unit cell, arranged around (0, $^1/_2$, $^1/_2$), ($^1/_2$, $^1/_2$, $^1/_2$), ($^1/_2$, 0, $^1/_2$), (0, 0, $^1/_2$), with the centers of gravity forming a rectangle with edges 4.409 and 4.554 Å. The closest intermolecular contacts are found from the carbonyl atoms to the centric C atoms of the neighboring molecule (O2 2.999, 2.938 Å; O12 2.801, 2.865 Å; O22′ 2.904, 2.994 Å; O32 2.836, 2.872 Å). The molecular planes are, however, tilted to each other (see Figure 5), thus forming interplanar angles to molecule I (numbering as given in Figure 4), by 83.4, 4.5, and 93.5°. The intramolecular distances and angles are comparable, so that mean values were calculated and are presented in Table 1. The values are found in normal ranges and agree fairly well with the data derived for the gas phase, except for the C—C bond length.

In the solid state (C—C = 1.551(3) Å) this bond is longer by 0.036(17) Å than that in the gas phase (1.515(17) Å). All calculated bond lengths are longer by 0.01−0.02 Å than the gas-phase values, and calculated angles agree with the experimental values to within ±2°.

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