

between Figures 10 and 11 constitutes strong evidence for the operation of corner-cutting tunneling even when the KIE value is modest. The many-body contributions to these KIEs will be the topic of a forthcoming publication.

The good agreement of the three-body molecular model with several aspects of the experimental data gives us some confidence that it provides a realistic description of the potential energy function in the regions near the saddle point and critical configurations. (One should, of course, not interpret the potential function quantitatively in other regions.)

## 6. Conclusions

From the dynamics modeling carried out in this work, we believe the following conclusions can be drawn.

(1) It is possible to model several important aspects of ion transfer reactions of complicated, polyatomic substances in solution by three-body potential functions. Such functions can be parameterized by trial-and-error fitting to experimental results combined with simple physically motivated analytic potential functions.

(2) In spite of its classical origins, phenomenological Marcus theory can give an excellent account of quantum-corrected results, even those dominated by multidimensional tunneling processes.

(3) Rate constants for hydride transfer between NAD<sup>+</sup> analogues can be successfully modeled in considerable quantitative detail by variational transition-state theory calculations in which most of the molecular transformations occur by corner-cutting tunneling processes. The most probable critical configurations have C-C distances significantly larger (>0.1 Å) than the C-C distances at the saddle points.

(4) The tightness parameter,  $\tau$ , correlates with the critical configuration C-C distance. It is a valid qualitative indicator of critical configuration tightness, although it is not quantitatively equal to the sum of the bond orders to the in-flight atom.

(5) The Marcus work terms,  $W^{\ddagger}$  and  $W^{\ddagger\ddagger}$ , are not identifiable with any specific feature of the potential energy surface. Neither in the present work nor in our earlier work<sup>4</sup> are there any structures which can be identified as precursor configurations.  $W^{\ddagger}$  and  $W^{\ddagger\ddagger}$  represent parts of the standard free energies of activation that do not correlate with the standard free energies of reaction.

**Acknowledgment.** The authors are grateful to Tomi Joseph, Thanh Truong, Gillian Lynch, and Da-hong Lu for assistance with the computations.

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# Gas-Phase Structure and Conformations of Malonyl Difluoride (COF-CH<sub>2</sub>-COF) and Difluoromalonyl Difluoride (COF-CF<sub>2</sub>-COF). An Electron Diffraction and ab Initio Study

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**Abstract:** The geometric structures and conformational compositions of malonyl difluoride, COF-CH<sub>2</sub>-COF (**1**), and difluoromalonyl difluoride, COF-CF<sub>2</sub>-COF (**2**), were studied by gas electron diffraction and ab initio calculations (HF/3-21G and HF/6-31G\*\*). The experimental scattering intensities of both compounds are reproduced best by mixtures of two conformers with aplanar skeletons and the C=O bonds eclipsed with respect to vicinal single bonds (C-C, C-H or C-F). The main conformer of **1** possesses C<sub>1</sub> symmetry with one COF group rotated by  $\delta_1(\text{CCCCO}) = 112(2)^\circ$  and the other COF group lying in the CCC plane ( $\delta_2(\text{CCCCO}) = 0^\circ$ , i.e. C=O cis to C-C). The presence of a small amount (10 (10)%) of a second conformer with C<sub>2</sub> symmetry and with both C=O bonds eclipsing the C-H bonds is likely. The relative stabilities of the two conformers of **2** are reversed. The low-energy form possesses C<sub>2</sub> symmetry with both COF groups rotated by  $120(2)^\circ$ , and the high-energy form (30 (15)%) possesses C<sub>1</sub> symmetry with one C=O bond eclipsing one vicinal C-F bond and the other C=O bond eclipsing the opposite C-C bond. The ab initio calculations predict the experimentally determined conformations with C<sub>1</sub> and C<sub>2</sub> symmetry to be stable structures, and their relative stabilities depend on the size of the basis set. The large basis set predicts the correct relative energies for **1** and the small basis set for **2**. Experimental bond lengths and bond angles are reproduced very well by the HF/3-21G method.

## Introduction

Over many years the keto-enol tautomerism, conformational properties, and structures of  $\beta$ -dicarbonyl compounds of the type COX-CH<sub>2</sub>-COX' have attracted considerable interest by experimentalists and theoreticians. A comprehensive review of these physical properties was given by Emsley.<sup>2</sup> In almost all  $\beta$ -dicarbonyls the U-cis enol form predominates, which is stabilized by intramolecular hydrogen bonding. Structures with asymmetric (C<sub>s</sub> symmetry) or symmetric hydrogen bonds (C<sub>2v</sub> symmetry) are considered in the literature. Assuming planarity of the carbon-

oxygen framework of the keto tautomer, three conformations are discussed: U-cis (Z,Z), W-trans (E,E), and S-trans (E,Z).

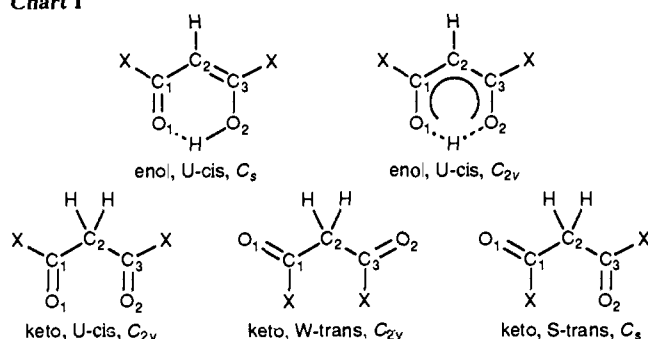
A considerable number of structural investigations of  $\beta$ -dicarbonyl compounds in the gas phase and in the crystal have been reported in the literature. The parent compound, malondialdehyde (MDA), with X = X' = H, was studied by microwave spectroscopy,<sup>3</sup> resulting in a planar enol U-cis structure of C<sub>s</sub> symmetry with a double minimum potential for the O-H...O hydrogen bond. This result has been reproduced by a number of theoretical calculations at various levels of sophistication.<sup>4-7</sup> Gas electron

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Chart 1



diffraction (GED) studies were performed for acetylacetone<sup>8-10</sup> (AA) and trifluoro-<sup>9</sup> and hexafluoroacetylacetone.<sup>11</sup> For the two latter compounds ( $X = \text{CH}_3$ ,  $X' = \text{CF}_3$  and  $X = X' = \text{CF}_3$ , respectively), the GED intensities were fitted with enol U-cis structures possessing  $C_{2v}$  symmetry. This implies a single minimum O...H...O hydrogen bond. The gas-phase structure of AA was investigated in three different laboratories. The most recent study by Iijima et al.<sup>8</sup> of the vapor at room temperature (>98% enol) results in a planar heavy atom skeleton of  $C_s$  symmetry, analogous to the structure of MDA. Such an unsymmetrical structure was also determined for the solid phase by X-ray diffraction.<sup>12</sup> In contrast to this result, Andreassen et al.<sup>9</sup> reported earlier a symmetrical ( $C_{2v}$ ) enol form for the room temperature vapor. Lowrey et al.<sup>10</sup> studied the composition and structure of both enol and keto tautomers, at 105 °C. The GED intensities were interpreted in terms of a mixture of 66 (5)% enol form with  $C_{2v}$  symmetry and 34 (5)% keto form with a slightly aplanar U-cis skeleton. In view of gas-phase thermodynamic data<sup>13</sup> (ca. 15% keto at 105 °C) the keto contribution obtained in the GED analysis appears to be overestimated. Since recent experimental and theoretical studies<sup>7</sup> favor strongly the asymmetric enol structure for AA, the above result for the keto tautomer should be taken with caution. Except for this study no other gas-phase structural investigation of a keto tautomer has been reported in the literature.

Similarly, almost all  $\beta$ -dicarbonyls, for which crystal structure investigations by X-ray or neutron diffraction have been performed, are enols, except for 1,3-diphenyl-2-methylpropane-1,3-dione and 1,3-diphenyl-2-(4-methoxyphenyl)propane-1,3-dione, COPh-CHR-COPh ( $R = \text{methyl}$  or 4-methoxyphenyl).<sup>14</sup> These two compounds adopt the keto form with an aplanar skeleton and carbonyl-carbonyl dihedral angles between 78° and 89°.<sup>15</sup> Whereas high-quality ab initio calculations have been reported for the enol tautomer of MDA, very scarce, rather low level, and contradicting theoretical results are found in the literature for the

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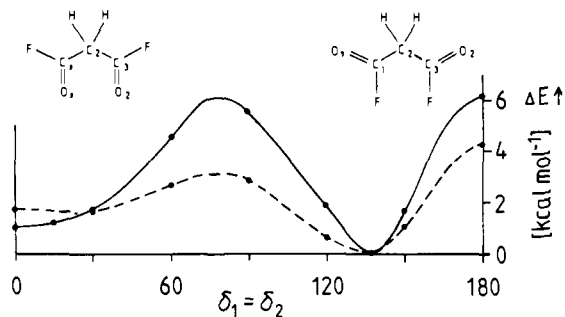
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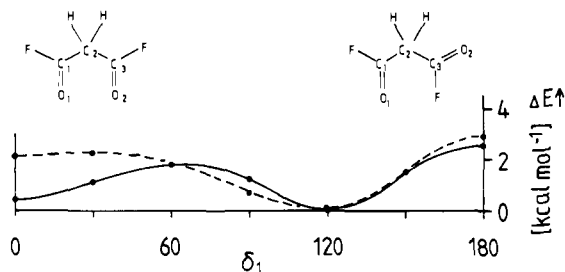
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(15) Reference 14 does not define the meaning of "carbonyl-carbonyl-dihedral" angles. We calculated the following dihedral angles  $\delta(\text{C1C2C3O})$  and  $\delta(\text{C3C2C1O})$  from the atomic coordinates in this publication: (90.7°, -20.0°) for the methyl compound, (-103.9°, 26.4°) and (-112.6°, 25.6°) for molecules 1 and 2 of the methoxyphenyl derivative. The opposite sign of the angles implies that both oxygen atoms lie on the same side of the C1C2C3 plane. The conformation of the skeleton is best described as S-gauche.



**Figure 1.** Calculated relative energies for various dihedral angles  $\delta_1$ - ( $\text{C1C2C3O2}$ ) =  $\delta_2$ ( $\text{C3C2C1O1}$ ) ( $C_2$  symmetry) of malonyl difluoride. Full line for HF/3-21G and broken line for HF/6-31G\*\*.



**Figure 2.** Calculated relative energies for various dihedral angles  $\delta_1$ - ( $\text{C1C2C3O2}$ ) with  $\delta_2$ ( $\text{C3C2C1O1}$ ) = 0 ( $C_1$  symmetry) for malonyl difluoride. Full line for HF/3-21G and broken line for HF/6-31G\*\*.

keto form. Ab initio calculations with the STO-3G basis set<sup>16</sup> predict the lowest energy conformation to be aplanar with CCCO dihedral angles of +138.5° and -1.9°. Full geometry optimization with a 4-31G basis set resulted in an aplanar near U-cis form with a carbonyl-carbonyl dihedral angle of 60°.<sup>17</sup> The semiempirical AM1 method predicts stable planar S-trans and W-trans conformations with the former being lower in energy by 0.5 kcal mol<sup>-1</sup>, whereas the MNDO approximation prefers an aplanar form of  $C_2$  symmetry with  $\delta(\text{CCCO}) = 77.9^\circ$ .<sup>7</sup>

The most interesting structural feature of  $\beta$ -diketones is the relative rotational orientation of the two carbonyl groups. In the two known crystal structures this orientation is affected by the bulky substituents at the  $\beta$ -carbons and by packing effects in the crystal. Furthermore, theoretical calculations for MDA do not give an unambiguous answer to this question. Therefore, it appears to be interesting to determine such relative orientations of carbonyl groups in the gas phase and we report here experimental and theoretical structural studies of malonyl difluoride (propanedioyl difluoride), COF-CH<sub>2</sub>-COF (1), and difluoromalonyl difluoride (2,2-difluoropropanedioyl difluoride), COF-CF<sub>2</sub>-COF (2). Both compounds are volatile and can be studied by GED. Furthermore, their conformations are not affected by steric requirements of their  $\beta$ -substituents. The NMR spectra<sup>18</sup> of 1 demonstrate that this  $\beta$ -dicarbonyl compound exists in the liquid phase only as the keto tautomer. In the <sup>1</sup>H spectrum there is only one proton signal at 3.8 ppm corresponding to the two methylene hydrogens, and no signal is observed in the range  $\delta = 10$ -18 ppm, where the enol protons are expected.<sup>2</sup> The gas-phase IR spectra, as well, give no indication for any contribution of the enol form in the vapor at room temperature. Typical vibrations for this form would be expected in the ranges 2600-3000 cm<sup>-1</sup> for the O-H...O vibration, 1560-1700 cm<sup>-1</sup> for the C=O vibration, and 1500-1630 cm<sup>-1</sup> for the C=C vibration.<sup>2</sup> In the range >1500 cm<sup>-1</sup>, there are no absorptions except those assigned to the keto form: 1866 cm<sup>-1</sup> (vvs, C=O); 2962 and 3003 cm<sup>-1</sup> (vww, symmetric and asymmetric CH<sub>2</sub>); 3722 cm<sup>-1</sup> (vw, 2 $\nu$ (C=O)). The higher stability

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**Table 1.** Optimized Geometries and Relative Energies for the Three Stable Conformations of Malonyl Difluoride (1)<sup>a</sup>

|  | S-gauche (C <sub>1</sub> symmetry) |         | W-gauche (C <sub>2</sub> symmetry) |         | U-cis              |                   |
|--|------------------------------------|---------|------------------------------------|---------|--------------------|-------------------|
|  | 3-21G                              | 6-31G** | 3-21G                              | 6-31G** | (C <sub>2v</sub> ) | (C <sub>2</sub> ) |
| C-H                                    | 1.082                              | 1.083   | 1.081                              | 1.082   | 1.085              | 1.084             |
| C1-C2                                  | 1.499                              | 1.504   |                                    |         |                    |                   |
| C1-C3                                  | 1.495                              | 1.505   | 1.498                              | 1.506   | 1.491              | 1.507             |
| C1-O1                                  | 1.180                              | 1.166   |                                    |         |                    |                   |
| C3-O2                                  | 1.181                              | 1.166   | 1.179                              | 1.165   | 1.178              | 1.164             |
| C1-F1                                  | 1.351                              | 1.318   |                                    |         |                    |                   |
| C3-F2                                  | 1.351                              | 1.317   | 1.354                              | 1.321   | 1.359              | 1.321             |
| C1C2C3                                 | 111.2                              | 112.0   | 109.6                              | 112.8   | 115.2              | 113.3             |
| HC2H                                   | 108.8                              | 108.4   | 109.6                              | 109.2   | 105.6              | 106.9             |
| C2C1O1                                 | 129.0                              | 127.9   | 129.2                              | 127.4   | 131.4              | 128.2             |
| C2C3O2                                 | 128.8                              | 127.0   |                                    |         |                    |                   |
| C2C1F1                                 | 109.6                              | 110.1   |                                    |         |                    |                   |
| C2C3F2                                 | 110.1                              | 111.1   | 109.5                              | 110.9   | 107.8              | 110.2             |
| δ <sub>1</sub> (C1C2C3O2)              | 123.8                              | 114.4   | 136.3                              | 134.3   | 0.0                | 27.1              |
| δ <sub>2</sub> (C <sub>3</sub> C2C1O1) | -12.8                              | -5.7    |                                    |         |                    |                   |
| ΔE/kcal mol <sup>-1</sup>              | 0.0                                | 0.0     | -0.6                               | +0.3    | +0.4               | +2.0              |

<sup>a</sup> For atom numbering see Figure 5.

of the keto form relative to the enol tautomer is also confirmed by our ab initio calculations (see below).

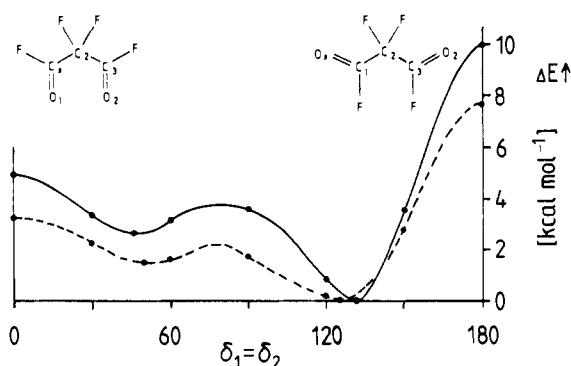
### Ab Initio Calculations

All calculations were performed with the GAUSSIAN 88 program package<sup>19</sup> (on a Cray 2 (RUS, Stuttgart) and on a Convex C2 (ZDV, Tübingen) computer) in the HF approximation and with 3-21G and 6-31G\*\* basis sets. The residual forces in the geometry optimizations were below  $3 \times 10^{-4}$  au. Whereas the shape of rotational potentials between atoms possessing lone pairs, such as for O-O bonds in peroxides<sup>20</sup> or N-N bonds in 2,3-diazabuta-1,3-butadiene<sup>21</sup> depends strongly on electron-correlation effects, it is generally assumed<sup>22</sup> that the shape of the potential functions for rotation around C-C bonds is reproduced correctly in the HF approximation.

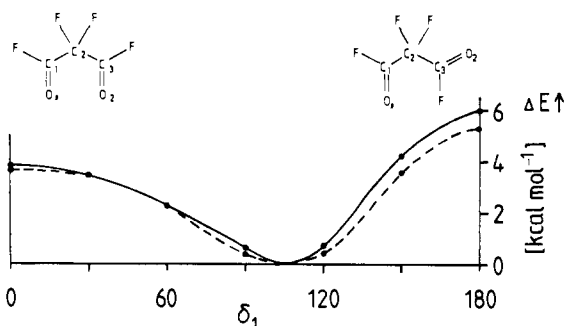
**Malonyl Difluoride (1).** In the first step, geometries with C<sub>2</sub> symmetry, i.e. both dihedral angles δ<sub>1</sub>(C1C2C3O2) and δ<sub>2</sub>(C3C2C1O1) are equal and have the same sign, were optimized with fixed δ<sub>1</sub> and δ<sub>2</sub> values in steps of 30°, with additional calculations at δ<sub>1</sub> = δ<sub>2</sub> = 15°. The gross shape of the potential curves (Figure 1) depends little on the size of the applied basis sets (3-21G and 6-31G\*\*). The only qualitative difference exists for the U-cis conformation, which is predicted to be exactly planar with the small basis set, whereas the larger basis results in a very shallow minimum for a slightly aplanar (pseudoplanar) structure. The absolute minimum for C<sub>2</sub> symmetry occurs at δ<sub>1</sub> = δ<sub>2</sub> = 136.3° (3-21G) and 134.3° (6-31G\*\*), respectively. This structure, which is best described as W-gauche, is lower in energy than the U-cis conformation by 1.0 kcal mol<sup>-1</sup> (3-21G) or 1.7 kcal mol<sup>-1</sup> (6-31G\*\*). The search for additional minima on the δ<sub>1</sub>δ<sub>2</sub>-energy hypersurface gave no stable structure of C<sub>1</sub> symmetry, i.e. δ<sub>1</sub> = -δ<sub>2</sub>.

Further geometry optimizations were performed for C<sub>1</sub> structures with δ<sub>2</sub> = 0° and varying δ<sub>1</sub> in steps of 30°. The corresponding relative energies are presented in Figure 2. The minima in these curves near δ<sub>1</sub> = 125° (3-21G) and 115° (6-31G\*\*) do not correspond to those for stable structures because of the constraint for δ<sub>2</sub>. The relative energies and geometric parameters of the fully optimized C<sub>1</sub> conformer, which can be described as S-gauche, are given in Table I, (together with the C<sub>2</sub> (C<sub>2v</sub>) structures. Calculations for the enol tautomer lead to a U-cis structure with C<sub>1</sub> symmetry as determined experimentally and theoretically for MDA (see Introduction). Depending on the basis set, the enol form of 1 is higher in energy than the most stable keto tautomer by 1.8 (3-21G) or 8.9 (6-31G\*\*) kcal mol<sup>-1</sup>.

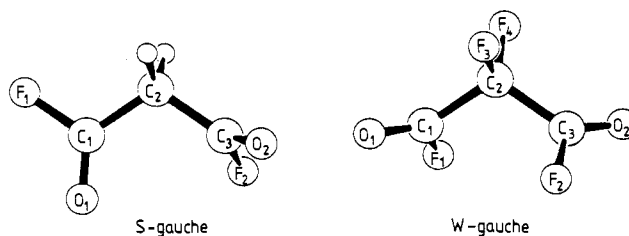
**Difluoromalonyl Difluoride (2).** The analogous computational procedures described above were applied to determine the stable conformers of this compound, as well (Figures 3 and 4). The potential function for



**Figure 3.** Calculated relative energies for various dihedral angles δ<sub>1</sub> - (C1C2C3O2) = δ<sub>2</sub>(C3C2C1O1) (C<sub>2</sub> symmetry) for difluoromalonyl difluoride. Full line for HF/3-21G and broken line for HF/6-31G\*.



**Figure 4.** Calculated relative energies for various dihedral angles δ<sub>1</sub> - (C1C2C3O2) with δ<sub>2</sub>(C3C2C1O1) = 0 (C<sub>1</sub> symmetry) for difluoromalonyl difluoride. Full line for HF/3-21G and broken line for HF/6-31G\*.



**Figure 5.** Molecular models with atom numbering of the main conformers of malonyl difluoride (S-gauche) and difluoromalonyl difluoride (W-gauche).

structures with C<sub>2</sub> symmetry possesses again the absolute minimum for a W-gauche conformation (δ<sub>1</sub> = δ<sub>2</sub> = 131.4° (3-21G) or 125.8° (6-31G\*\*), respectively) and a second minimum for a nonplanar U-gauche

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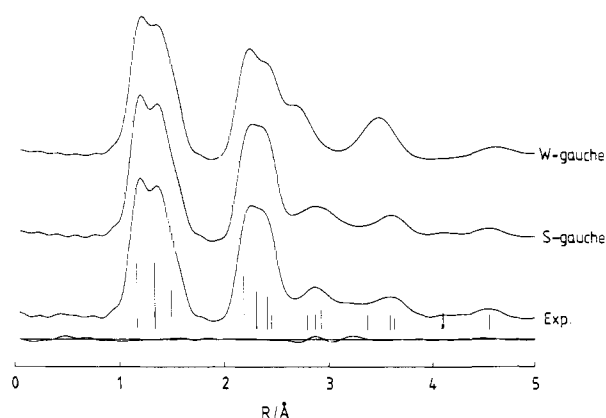
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**Table II.** Optimized Geometries and Relative Energies for the Three Stable Conformations of Difluoromalonyl Difluoride (2)<sup>a</sup>

|                                    | S-gauche ( $C_1$ symmetry) |        | W-gauche ( $C_2$ symmetry) |        | U-gauche ( $C_2$ symmetry) |        |
|------------------------------------|----------------------------|--------|----------------------------|--------|----------------------------|--------|
|                                    | 3-21G                      | 6-31G* | 3-21G                      | 6-31G* | 3-21G                      | 6-31G* |
| C2-F3                              | 1.357                      | 1.322  |                            |        |                            |        |
| C2-F4                              | 1.357                      | 1.330  | 1.356                      | 1.323  | 1.357                      | 1.326  |
| C1-C2                              | 1.515                      | 1.526  |                            |        |                            |        |
| C1-C3                              | 1.506                      | 1.528  | 1.508                      | 1.528  | 1.516                      | 1.534  |
| C1-O1                              | 1.178                      | 1.164  |                            |        |                            |        |
| C3-O2                              | 1.173                      | 1.160  | 1.172                      | 1.159  | 1.178                      | 1.163  |
| C1-F1                              | 1.333                      | 1.302  |                            |        |                            |        |
| C2-F2                              | 1.342                      | 1.306  | 1.345                      | 1.312  | 1.332                      | 1.300  |
| C1C2C3                             | 109.5                      | 111.7  | 109.0                      | 112.4  | 109.4                      | 110.1  |
| F3C2F4                             | 109.3                      | 108.9  | 110.2                      | 109.6  | 109.4                      | 108.7  |
| C2C1O1                             | 124.5                      | 125.0  |                            |        |                            |        |
| C2C3O2                             | 128.2                      | 125.7  | 129.0                      | 126.7  | 124.0                      | 123.2  |
| C2C1F1                             | 111.8                      | 110.8  |                            |        |                            |        |
| C2C3F2                             | 108.1                      | 109.9  | 107.4                      | 109.2  | 112.4                      | 112.6  |
| $\delta_1$ (C1C2C3O2)              | 118.2                      | 109.1  |                            |        |                            |        |
| $\delta_2$ (C3C2C1O1)              | -24.3                      | -7.8   | 131.4                      | 125.8  | 46.4                       | 50.5   |
| $\Delta E$ /kcal mol <sup>-1</sup> | 0.0                        | 0.0    | -1.0                       | +0.4   | +1.7                       | +1.9   |

<sup>a</sup>For atom numbering see Figure 5.**Figure 6.** Experimental and calculated radial distribution functions and difference curve for malonyl difluoride. The positions of the interatomic distances of the main conformer are indicated by vertical bars. Distances involving hydrogens are omitted.

form ( $\delta_1 = \delta_2 = 46.4^\circ$  or  $50.5^\circ$ ). The fully optimized geometry of the  $C_1$  form is again an S-gauche structure. The geometries and relative energies of the three stable conformers are collected in Table II.

### Experimental Structure Analyses

**Malonyl Difluoride (1).** Model calculations for a large number of conformations demonstrate that the experimental radial distribution function (Figure 6) can be reproduced reasonably well only with an S-gauche conformer. This finding confirms the result of the HF/6-31G\*\* calculations which predict this form to be lower in energy than the W-gauche conformation in contrast to the HF/3-21G prediction. The agreement between experimental and calculated radial distribution functions is slightly improved if a small contribution of a W-gauche conformer with  $\delta(\text{CCCO})$  around  $135^\circ$  is added. The inclusion of a small amount (<10%) of a U-cis or U-gauche form does not lead to a further improvement, and larger amounts of the latter deteriorate the fit. Therefore, only S-gauche and W-gauche conformers were considered in the experimental analysis, although the ab initio calculations predict three stable structures. The preliminary structure model for the S-gauche form was then refined by a least-squares procedure of the molecular intensities. These were modified with a diagonal weight matrix and scattering amplitudes and phases of Haase were used.<sup>23</sup> Both COF groups were assumed to have equal geometric parameters, except for the two dihedral angles.  $\delta_1$  was refined and  $\delta_2$  was set to zero. Vibrational amplitudes for closely spaced interatomic distances were collected in groups, and further constraints are evident from Table III. All bond lengths,

**Table III.** Results of the Electron Diffraction Analysis for Malonyl Difluoride (1)

| Geometric Parameters for the S-Gauche Conformer <sup>a</sup> |                    |                      |                  |
|--|--------------------|----------------------|------------------|
| C—H  | 1.10 <sup>b</sup>  | C—C=O                | 129.1 (8)        |
| C—C  | 1.502 (5)          | C—C—F                | 109.7 (7)        |
| C=O  | 1.177 (3)          | F—C=O <sup>c</sup>   | 121.2 (11)       |
| C—F  | 1.349 (4)          | $\delta_1$ (C1C2C3O) | 112.0 (20)       |
| C—C—C  | 110.2 (10)         | $\delta_2$ (C3C2C1O) | 0.0 <sup>b</sup> |
| H—C—H  | 108.0 <sup>b</sup> | % W-gauche           | 10 (10)          |

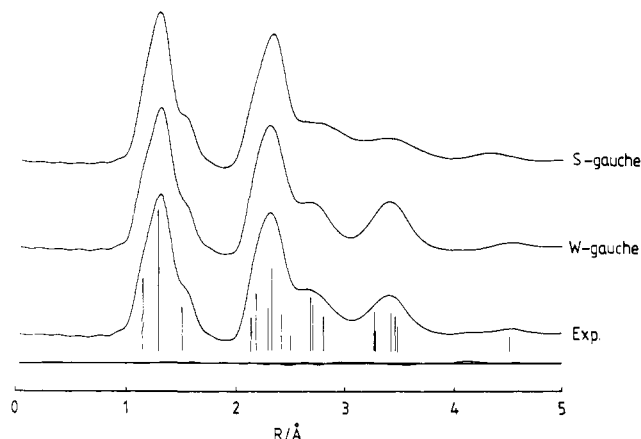
  

| Interatomic Distances and Vibrational Amplitudes for the S-Gauche Conformer (without distances involving hydrogens) |      |                   |          |
|---|------|-------------------|----------|
| C=O   | 1.18 | 0.036 (3)         | $\ell_1$ |
| C—F   | 1.35 | 0.044 (4)         | $\ell_2$ |
| C—C   | 1.50 | 0.056 (6)         | $\ell_3$ |
| F1...O1   | 2.20 | 0.050 (8)         | $\ell_4$ |
| C2...F1   | 2.33 |                   |          |
| C2...O1   | 2.42 | 0.053 (12)        | $\ell_5$ |
| C1...C3   | 2.46 |                   |          |
| C3...O1   | 2.81 |                   |          |
| C1...F2   | 2.89 | 0.18 (3)          | $\ell_6$ |
| O1...F2   | 2.94 |                   |          |
| C1...O2   | 3.38 | 0.15 <sup>b</sup> |          |
| O1...O2   | 3.61 | 0.12 (2)          | $\ell_7$ |
| C3...F1   | 3.65 |                   |          |
| F1...F2   | 4.10 | 0.18 (4)          | $\ell_8$ |
| F1...O2   | 4.55 |                   |          |

<sup>a</sup> $r_a$  distances in Å and  $\angle_a$  angles in deg. Error limits are  $3\sigma$  values and include a possible scale error of 0.1%. For atom numbering see Figure 5. <sup>b</sup>Not refined. <sup>c</sup>Dependent parameter.

angles, and vibrational amplitudes of the W-gauche form were set equal to those of the main S-gauche conformer, and the HF/6-31G\*\* value was used for the dihedral angles ( $\delta_1 = \delta_2 = 134^\circ$ ). With these assumptions seven geometric parameters and eight vibrational amplitudes were refined simultaneously. Least-squares analyses with fixed but different values for the W-gauche:S-gauche ratio give a minimum of the  $R$ -factor for a contribution of 10 (10)% W-gauche. The estimated uncertainty corresponds to an increase of the  $R$ -factor by 5%. The following correlation coefficients had values larger than |0.6|: CCO/CCF = -0.90, CCF/ $\ell_5$  = 0.84,  $\ell_1/\ell_3$  = 0.62. The numbering of the vibrational amplitudes  $\ell_i$  and the final results are given in Table III.

**Difluoromalonyl Difluoride (2).** The experimental radial distribution function for this compound (Figure 7) is reproduced best with a structural model possessing  $C_2$  symmetry and CCCO dihedral angles around  $120^\circ$  (W-gauche). The agreement between calculated and experimental curves in the range  $r > 2.8$  Å improves if the presence of a second conformer of S-gauche form is allowed for. Inclusion of a U-gauche conformer does not improve the agreement. The least-squares analysis was performed analogous to that for 1. The C—F distances of the carbonyl group (C—F<sub>c</sub>)



**Figure 7.** Experimental and calculated radial distribution functions and difference curve for difluoromalonyl difluoride. The positions of the interatomic distances of the main conformer are indicated as vertical bars. The  $(C-F)_{\text{mean}}$  bond distance is shown.

and of the methylene group ( $C-F_m$ ) could not be refined independently. The difference  $\Delta CF = (C-F_c) - (C-F_m)$  was fixed at a value predicted by the ab initio calculations (Table II) and an uncertainty of 0.01 Å is estimated for this difference. All geometric parameters of the S-gauche form were constrained to those for the major W-gauche conformer, except for the dihedral angles, which were set to the ab initio values ( $\delta_1 = 109^\circ$ ,  $\delta_2 = -8^\circ$ ). With these assumptions eight geometric parameters and seven vibrational amplitudes were refined simultaneously. The following correlation coefficients had values larger than |0.6|:  $CCC/FCF = -0.69$ ,  $CCC/CCO = -0.62$ ,  $CCO/\ell_4 = -0.90$ ,  $\delta/\ell_6 = 0.64$ . Numbering of the vibrational amplitudes  $\ell_i$  and the results of the final least-squares analysis are given in Table IV.

### Discussion

According to the GED analyses the vapor of both dicarbonyl compounds consists of two conformers at room temperature. The gas-phase IR spectra give no indication of such a mixture. In contrast to other carbonyl compounds studied in our laboratory, such as  $FC(O)NCO$ ,<sup>24</sup>  $FC(O)SCl$ ,<sup>25</sup>  $(FC(O)S)_2$ ,<sup>26</sup> and  $(FC(O)O)_2$ ,<sup>26</sup> where the presence of two conformers is clearly indicated by splitting of the  $C=O$  vibrations by 20–40  $cm^{-1}$ , only one sharp band is observed in the gas-phase IR spectra of the dicarbonyls.

In malonyl difluoride (1) the main component is the S-gauche conformer ( $C_1$  symmetry) with a possible small contribution of a W-gauche ( $C_2$  symmetry) form. Considering the different degeneracy of both structures, the experimentally determined contribution (10 (10)%) corresponds to a free enthalpy difference  $\Delta G = G(W\text{-gauche}) - G(S\text{-gauche}) > 0.4$  kcal mol<sup>-1</sup>. In the ab initio calculations the relative stability of these two conformations depends on the basis set  $\Delta E = E(W\text{-gauche}) - E(S\text{-gauche}) = -0.6$  kcal mol<sup>-1</sup> for 3-21G and  $\Delta E = +0.3$  kcal mol<sup>-1</sup> for 6-31G\*\*. Assuming that the differences in the zero-point vibrations and in the entropies are small,<sup>25</sup> the value obtained with the larger basis set is in good agreement with experiment.

The same types of conformers are also present in the vapor of the difluoro derivative (2), but here, according to the GED analysis, the W-gauche form predominates (70 (15)%) over the S-gauche structure (30 (15)%). This ratio corresponds to  $\Delta G = G(W\text{-gauche}) - G(S\text{-gauche}) = -0.9$  (4) kcal mol<sup>-1</sup>. (For systematic reasons  $\Delta G$  is defined the same way for 1 and 2.) Again, the small basis set predicts the W-gauche form to be lower in energy than the S-gauche form ( $\Delta E = E(W\text{-gauche}) - E(S\text{-gauche}) = -1.0$  kcal mol<sup>-1</sup>) and the larger 6-31G\* basis set predicts the S-gauche form to be predominating ( $\Delta E = +0.4$  kcal mol<sup>-1</sup>). In contrast to 1, where the experimental conformational com-

**Table IV.** Results of the Electron Diffraction Analysis for Difluoromalonyl Difluoride (2)

| Geometric Parameters for the W-Gauche Conformer <sup>a</sup> |                        |                    |            |
|--|------------------------|--------------------|------------|
| $(C-F)_{\text{mean}}$  | 1.328 (2)              | C—C—C              | 110.6 (5)  |
| $\Delta CF = (C-F_c) - (C-F_m)^b$                            | -0.02 [1] <sup>c</sup> | $F_m-C-F_m$        | 107.9 (7)  |
| $C-F_c^d$  | 1.323 (6)              | C—C=O              | 128.2 (7)  |
| $C-F_m$  | 1.333 (6)              | C—C—F <sub>c</sub> | 107.7 (5)  |
| C—C  | 1.531 (4)              | $F_c-C=O^d$        | 124.1 (9)  |
| C=O  | 1.168 (3)              | $\delta(CCCO)$     | 120.0 (16) |
|  |                        | % S-gauche         | 30 (15)    |

Interatomic Distances and Vibrational Amplitudes for the W-Gauche Conformer

|                  |      |           |          |
|------------------|------|-----------|----------|
| C=O              | 1.17 | 0.041 (3) | $\ell_1$ |
| C—F <sub>c</sub> | 1.32 | 0.050 (3) | $\ell_2$ |
| C—F <sub>m</sub> | 1.33 |           |          |
| C—C              | 1.53 | 0.048 (4) | $\ell_3$ |
| F3...F4          | 2.16 |           |          |
| O1...F1          | 2.20 | 0.059 (5) | $\ell_4$ |
| C2...F1          | 2.31 |           |          |
| C1...F3          | 2.34 |           |          |
| C2...O1          | 2.43 |           |          |
| C1...C3          | 2.52 | 0.20 (4)  | $\ell_5$ |
| F1...F3          | 2.70 |           |          |
| O1...F4          | 2.72 |           |          |
| C1...F2          | 2.82 |           |          |
| F1...F2          | 3.29 | 0.21 (3)  | $\ell_6$ |
| O1...F3          | 3.29 |           |          |
| O1...F2          | 3.43 |           |          |
| F1...F4          | 3.46 |           |          |
| C3...O1          | 3.47 | 0.13 (3)  | $\ell_7$ |
| O1...O2          | 4.52 |           |          |

<sup>a</sup>  $r_a$  distances in Å and  $\angle_a$  angles in deg. Error limits are  $3\sigma$  values and include a possible scale error of 0.1%. For atomic numbering see Figure 5. <sup>b</sup>  $F_c$ , carbonyl fluorine;  $F_m$ , methylene fluorine. <sup>c</sup> Not refined, but varied within the range in square brackets. <sup>d</sup> Dependent parameter. <sup>e</sup> Not refined.

position is in agreement with the HF/6-31G\*\* calculations, the experimental result for 2 is reproduced better by the small basis set ( $\Delta G = -0.9$  (4) kcal mol<sup>-1</sup> and  $\Delta E = -1.0$  kcal mol<sup>-1</sup>).

### Conclusion

The electron diffraction intensities of malonyl difluoride (1) and difluoromalonyl difluoride (2) are reproduced best by mixtures of two conformers, S-gauche/W-gauche for 1 and W-gauche/S-gauche for 2, all of which have nonplanar skeletons. They are characterized by eclipsed positions of the  $C=O$  double bonds relative to vicinal single bonds. In the W-gauche structure both  $C=O$  bonds eclipse  $C-H$  or  $C-F$  bonds of the methylene group, and in the S-gauche form one  $C=O$  bond eclipses a methylene bond and the other the opposite  $C-C$  bond. Apparently the U-cis form with both  $C=O$  bonds eclipsing the opposite  $C-C$  bonds is destabilized by a repulsive  $O...O$  interaction. Conformations with carbonyl  $C-F$  bonds eclipsing opposite  $C-C$  bonds, i.e. S-trans and W-trans, do not form stable structures but correspond to maxima on the potential curves (Figures 1–4). It is unsatisfactory that ab initio calculations predict the correct main conformer of 1 if a large basis set is used, whereas the correct main conformer of 2 is predicted with a small basis set, although both molecules are very similar. On the other hand, the relevant energy differences are smaller than 1.5 kcal mol<sup>-1</sup>.

### Experimental Section

Gas-phase IR spectra were recorded in the range 4000–400  $cm^{-1}$  with a Bomem MB-100 spectrometer, mass spectra were recorded with a Finnigan MAT 8230, 70 eV, spectrometer, and NMR spectra were recorded with Bruker AC 80 (<sup>1</sup>H, <sup>19</sup>F) and WH 360 (<sup>13</sup>C) spectrometers. Reagents: malonic acid (Janssen, 99%), SF<sub>4</sub> prepared by a literature method,<sup>27</sup> F<sub>2</sub> (Kali Chemie), and NaF (Merck, 99%).

Malonyl difluoride (1) was obtained by a modified procedure described earlier.<sup>28</sup> Into a 300-mL Monel vessel containing premixed malonic acid

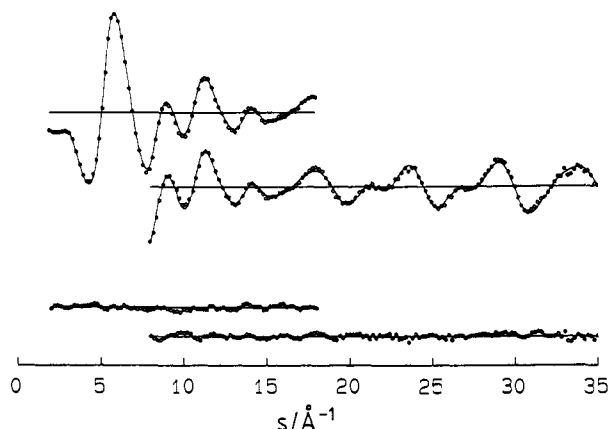
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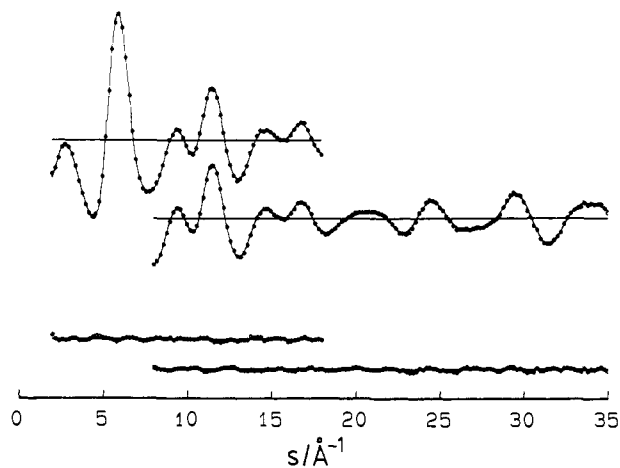
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**Figure 8.** Experimental (dots) and calculated (full line) molecular intensities and differences for malonyl difluoride.



**Figure 9.** Experimental (dots) and calculated (full line) molecular intensities and differences for difluoromalonyl difluoride.

(20.0 g, 192.2 mmol) and NaF (20.0 g, 476.3 mmol), 56.4 g of SF<sub>4</sub> (522.0 mmol) are added by condensation at -196 °C. After being warmed to room temperature the vessel is kept at +60 °C for 72 h. A vacuum trap-to-trap condensation (0, -78, -196 °C) yields 19.0 g of **1** (175.9 mmol, 91.5%) as a colorless crystalline solid in the -78 °C trap. **1**, when stored at -20 °C or above in a Pyrex vessel, develops a yellow

color due to an involatile impurity of unknown nature. IR (gas): 3722 (vw), 3003 (vvw), 2962 (vvw), 1866 (vs), 1411 (m), 1346 (s), 1241 (s), 1151 (s), 1111 (vs), 956 (w), 862 (s), 725 (m), 623 (s), 562 (m) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 3.8 ppm (t, <sup>3</sup>J<sub>HF</sub> = 1.4 Hz). <sup>19</sup>F NMR (CDCl<sub>3</sub>): δ = 47.9 ppm (t, <sup>3</sup>J<sub>FF</sub> = 1.4 Hz, <sup>4</sup>J<sub>FF</sub> = 17.2 Hz, from <sup>13</sup>C-satellites, d, d, t). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ<sub>CH<sub>2</sub></sub> = 36.9 ppm (t, t, <sup>1</sup>J<sub>CH</sub> = 135.0 Hz, <sup>2</sup>J<sub>CF</sub> = 62.4 Hz), δ<sub>COF</sub> = 154.1 ppm (d, t, d, <sup>1</sup>J<sub>CF</sub> = 357.3 Hz, <sup>2</sup>J<sub>CH</sub> = 8.8 Hz, <sup>3</sup>J<sub>CF</sub> = 7.1 Hz). The <sup>19</sup>F and <sup>13</sup>C shifts are in good agreement with those of ref 18.

**2,2-Difluoromalonyl Difluoride (2).** **1** (12.1 g, 112 mmol) was condensed into a 1-L Monel vessel containing 18.0 g of NaF (429 mmol) at -196 °C. The vessel was connected to a stainless steel vacuum line and maintained at 0 °C. Under control of the internal pressure F<sub>2</sub> was added at a rate of ca. 0.1 g/h. When the total pressure of products reached 450 mbar, addition of F<sub>2</sub> was stopped. Fractional condensation in vacuo through -78, -130, and -196 °C cold traps yields 1.7 g of **2** (11.8 mmol 10.5%) in the -130 °C trap as a colorless solid: mp -99 °C. IR(gas): 1894 (vs), 1289 (s), 1220 (s), 1186 (s), 1111 (s), 1014 (s), 777 (w), 737 (m), 681 (w), 587 (vw), 481 (vw) cm<sup>-1</sup>. <sup>19</sup>F NMR (CDCl<sub>3</sub>): δ<sub>CF<sub>2</sub></sub> = -111.5 (t, <sup>3</sup>J<sub>FF</sub> = 10.6 Hz), δ<sub>COF</sub> = +21.5 (t, <sup>4</sup>J<sub>FF</sub> = 3.7 Hz, from <sup>13</sup>C satellites, d, t, d). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ<sub>CF<sub>2</sub></sub> = 103.5 ppm (t, t, <sup>1</sup>J<sub>CF</sub> = 266.6 Hz, <sup>2</sup>J<sub>CF</sub> = 81.4 Hz), δ<sub>COF</sub> = 148.4 ppm (d, t, <sup>1</sup>J<sub>CF</sub> = 376.1 Hz, <sup>2</sup>J<sub>CF</sub> = 35.6 Hz). MS, *m/z* (%) 144 (1), 97 (42), 78 (32), 69 (72), 50 (14), 47 (100).

The GED intensities were recorded with a Balzers Gasdiffractograph<sup>29</sup> at two camera distances (25 and 50 cm) and with an accelerating voltage of ca. 60 kV. The electron wavelength was determined from ZnO powder patterns. The sample reservoirs were kept at 20 °C (**1**) and -68 °C (**2**), and the stainless steel inlet system and nozzle were maintained at room temperature. The camera pressure during the diffraction experiments was below 2 × 10<sup>-5</sup> mbar. Two photographic plates for each compound and camera distance were analyzed by the usual procedures.<sup>30</sup> Numerical values of the total scattering intensities in the *s* ranges 2–18 and 8–35 Å<sup>-1</sup> in steps of Δ*s* = 0.2 Å<sup>-1</sup> are available as supplementary material. The averaged molecular intensities are presented in Figures 8 and 9.

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**Registry No.** **1**, 870-75-7; **1** enolate, 135468-32-5; **2**, 5930-67-6.

**Supplementary Material Available:** Tables of total intensities for malonyl difluoride and difluoromalonyl difluoride (3 pages). Ordering information is given on any current masthead page.

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