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Blue-Shifting Intramolecular C−H···O Interactions

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Two model systems, 3-methylacroleine and 3-(difluoromethyl)acroleine, are investigated computationally with respect to the character of the C−H···O interaction in their chelate-type (ZZ) conformers. By selecting the appropriate reference conformers, the C−H···O interaction is shown to result in the increase of the C−H stretching frequency (i.e., in the blue shift of the C−H stretching band). This is accompanied by the shortening of the C−H bond distance as compared to its values in reference molecules. Parallel to calculations of the C−H bond distance and stretching frequency, the energy contribution of the C−H···O interaction to the total energy (i.e., the energy associated with the C−H···O contact) is evaluated by using the methods proposed recently for the estimation of the energies of intramolecular hydrogen bonds. It is found that the C−H···O contact in the chelate-type forms of 3-methylacroleine and 3-(difluoromethyl)acroleine corresponds to the negative energy contribution and is repulsive. It is concluded that, despite the stability of the ZZ conformers of the two molecules and their deceptive structural shape, no hydrogen bond in the usual sense is formed between the C−H bond and the lone pair donor. The results are interpreted in terms of the steric compression, which leads to the dominance of the valence repulsion contribution in the C−H···O contact. This mechanism suggests that blue-shifting intramolecular interactions should not be that uncommon, although their recognition requires a careful consideration of the reference system.

I. Introduction

In recent years a great deal of attention has been given to what is currently referred to as the improper, blue-shifting hydrogen bonds.[1−4] For certain pairs of bonds (X−H) and lone pair donors (Y) their mutual interaction (X−H···Y) has been found to result in spectroscopic effects[5−8] opposite to those observed for the usual (traditional) hydrogen bonds.[9] The structural similarity of the interaction pattern to that of the usual hydrogen bridge turned out to be quite deceptive, and considerable effort has been made to explain the origin of differences between traditional and improper hydrogen bonds.[4,10−22]

The most plausible explanation of these differences[12,14] refers to a subtle interplay between the attractive electrostatic forces and valence repulsion. The first of these factors is dominant for traditional hydrogen bonds and leads to large red shifts of the X−H stretching frequency. The valence repulsion alone would lead to the compression of the X−H bond and shift the X−H stretching frequency upward. This mechanism of the blue shift of the X−H stretching frequency suggests that the corresponding effect should be enhanced by sterically induced compression of the X−H···Y bridge, which may arise in the case of intramolecular hydrogen bonds. Indeed this has been found long ago by Pinchas,[23−26] who observed the increase of the C−H stretching frequency in *o*-nitrobenzaldehyde and in structurally similar *o*-alkoxybenzaldehydes and suggested that it originates from the intramolecular C−H···O bonding. Surprisingly enough, Pinchas does not seem to have seen anything particularly peculiar in the increase of the C−H stretching frequency.[26] According to his interpretation, the increase of the C−H stretching frequency is *due to the hydrogen bonding* between C−H and the oxygen atom of the nitro group.

Recently the effect of the sterically induced compression of intramolecular X−H···Y contacts (bonds) has been investigated by Li et al.[12] and Fang et al.[27] Their computational studies indicate that the blue shift of the X−H stretch due to certain types of intramolecular X−H···Y contacts may not be that uncommon. However, to establish the direction of the shift of the X−H stretching frequency one needs some well-defined reference value. For intermolecular X−H···Y bonds this reference frequency is supplied by the isolated subsystem X−H. In the case of intramolecular X−H···Y interactions, the reference frequency is at least a little ambiguous; the intramolecular X−H···Y contact cannot be removed without significant changes in the structure of the system as a whole. The breaking of the intramolecular X−H···Y contact can be achieved, for instance, by changing the conformation of the system. Then, however, the corresponding “free” X−H bond becomes embedded in a different environment, which may also lead to some changes in the X−H stretching frequency. The changes of the X−H stretching frequency due to traditional intramolecular hydrogen bonds[28] are usually large enough to make the choice of the reference value almost insignificant. The corresponding red shifts can be established with only a little ambiguity. The blue shifts due to improper X−H···Y interactions are usually small. Hence, the identification of the blue shift due to intramolecular X−H···Y contacts may significantly depend on the assumed reference.

One should also note that the direct intramolecular X−H···Y contact that follows from the determination of the molecular geometric structure and formally looks as the X−H···Y bond is not necessarily related to the attractive interaction between X−H and Y. The presence of the intramo-

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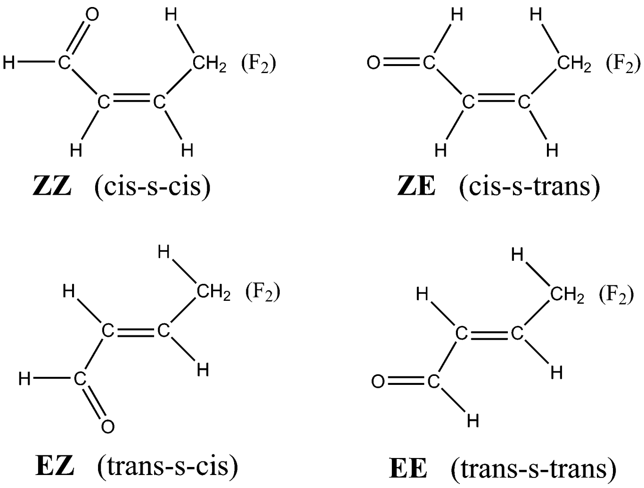

Figure 1. Four conformations of 3-methylacroleine [3-(difluoromethyl)acroleine]. The explanation of the conformer labels.

lecular X−H···Y contact corresponds to a local minimum on the full potential energy surface of the given molecule. The X−H···Y region can be either attractive or repulsive. The repulsive character of this region can be compensated by the energy lowering due to other changes in the molecule. If a bond in a polyatomic molecule is meant to be a feature that makes the energy of the intramolecular X−H···Y unit lower than that which one would expect for an abstract system with noninteracting X−H and Y units at the same molecular geometry, some of intramolecular X−H···Y contacts may not conform to this definition. Actually, though reported as a positive number, the negative value of the energy of the C−H...O bond in *o*-nitrobenzaldehyde follows from the early measurements by Pinchas.[26] According to his data the energy of the C−H···O bond in *o*-nitrobenzaldehyde can be estimated as −2 kcal/mol.[29] One can conclude that the C−H···O contact in this molecule *does not* give a bonding contribution to the total molecular energy and, hence, is not a hydrogen bond in the usual sense.

The present study is intended to further[12,27] investigate the blue-shifting intramolecular C−H···O(=C) contacts in model systems and to discuss these contacts in terms of "bond" energies. Two model molecules, 3-methylacroleine (but-2-enal) and 3-(difluoromethyl)acroleine (4,4-difluorobut-2-enal), will be investigated computationally. These molecules may exist in several conformations, and four of them are considered in this study. By their mutual comparison one can establish the most likely reference frequency for the C−H stretching vibration in the system with the C−H···O(=C) contact and predict direction of the interaction−induced frequency shift. Another advantage of the present model molecules follows from the possibility of the estimation of the energy related to the C−H···O(=C) intramolecular interaction by using methods devised in our recent paper.[30]

A brief account of computational details of the present study is given in Section II, and the main energy and structural data will be analyzed in Section III. Our attention will be primarily focused on the following two problems. The first is the estimation of the frequency shift of the C−H vibration with respect to some reference C−H unit whose choice will be discussed and facilitated by the study of different conformers (see Figure 1). The corresponding data will be presented and discussed in Section IV. These frequency data will be also supplemented by the analysis of the relevant C−H bond distances. The second main issue, which is considered in Section V, is the estimation of the energy of the C−H···O(=C) bond. For this purpose, we shall use two methods developed in our recent study[30] of the energy of intramolecular hydrogen bonds. The meaning of the estimated C−H···O(=C) bond energy will be discussed. A summary of our investigations and conclusions are presented in Section VI.

II. Computational Details

All calculations reported in this paper have been carried out at the level of the second-order perturbation theory (MP2) approximation for electron correlation effects by using computer programs of Gaussian03.[31] In correlated MP2 calculations, all 1s core orbitals have been frozen. For all investigated conformers of the two molecules, their geometry was optimized either without constraints or under the assumption of their flatness (i.e., with the constraint of planarity of the C−C=C−C=O skeleton). Since some of the changes of the geometry parameters between different conformers turned out to be very small, the corresponding calculations have been repeated with tighter than default convergence thresholds and different starting geometries. This refers particularly to the evaluation of the so-called tilt angle (see Section III). The four studied conformers are schematically shown in Figure 1 and correspond to what is called ZZ (*cis*−*s*-*cis*), ZE (*cis*−*s*-*trans*), EZ (*trans*−*s*-*cis*), and EE (*trans*−*s*-*trans*) forms of the skeleton. To avoid the mechanical coupling of different C−H stretching vibrations, the relevant C−H stretching frequency has been calculated for deuterated species in which all but one hydrogen was substituted by deuterium.

At variance with the majority of calculations on blue-shifting systems, which are carried out with Pople's Gaussian basis sets,[31] the present study uses systematic sequences of correlation consistent (cc-pVXZ) and augmented correlation consistent (*aug*-cc-pVXZ) sets of Dunning et al.[32,33] The X values correspond to 2ζ (X = D) and 3ζ (X = T) quality of Dunning's basis sets. The use of these bases permits to study the stability of our results with respect to the systematic basis set extension. To resolve some uncertainties with respect to the calculated minimum energy structures (vide infra) selected calculations have been also performed with the cc-pVQZ basis set.

III. Energies and Selected Structural Data

The plain energy data for all optimized structures of 3-methylacroleine and 3-(difluoromethyl)acroleine are presented in Tables 1 and 2, respectively. For the reference ZZ conformer, the absolute energy data (in au) are given whereas for all other conformers C, C = ZE, EZ, and EE; only the relative energies (in kcal/mol), $E^{\mathrm{C}}-E^{\mathrm{ZZ}}$, are presented. The full optimization of molecular geometries shows that the ZE, EZ, and EE conformers are all quasi-planar (i.e., all nuclei, except for the two hydrogen (fluorine) atoms of the CH$_3$ (CHF$_2$) group, lie in the same plane). This result is independent of the basis set used in calculations. One should also note that for both studied systems the lowest energy conformation is represented by the most elongated EE structure. All other fully optimized structures correspond to local minima on the energy hypersurface. The barriers to the internal rotation about single HOC−CH= and double −CH=CH− bonds are, however, high enough to stabilize the local minima for all investigated conformers. This has been verified by performing MP2/*aug*-cc-pVTZ calculations for the optimized structure with the HOC− group in the ZZ conformer twisted by 90°. The energy increase amounts to 5.15 and 4.77 kcal/mol in 3-methylacroleine and 3-(difluoromethyl)acroleine, respectively, and is considerably larger than the energy differences between optimized ZZ and ZE conformers (see Tables 1 and 2).

TABLE 1: Energies (in kcal/mol) of Different Structures of 3-Methylacroleine Relative to the ZZ Conformer Calculated in the MP2 Approximation with Different Correlation Consistent Basis Sets[a]

	basis set			
conformer	cc-pVDZ	cc-pVTZ	*aug*-cc-pVDZ	*aug*-cc-pVTZ
fully optimized structures				
ZZ	−230.535331	−230.764032	−230.577533	−230.780938
	(−230.460919)	(−230.689791)	(−230.504022)	(−230.706902)
ZE	+0.13	−0.83	−1.06	−1.18
	(+0.06)	(−0.76)	(−0.99)	(−1.09)
EZ	−1.62	−1.67	−1.70	−1.57
	(−1.68)	(−1.68)	(−1.64)	(−1.61)
EE	−2.80	−3.61	−3.98	−3.87
	(−2.95)	(−3.62)	(−3.86)	(−3.86)
fictitious structures[b]				
EZ	−0.43	−0.50	+0.06	−0.20
EE	−1.33	−1.89	−1.73	−1.82
flat optimized structure[c]				
ZZ	−230.535331	−230.764023	−230.577426	−230.780840
ZE	+0.13	−0.84	−1.13	−1.24
fictitious flat structures[d]				
EZ	−0.43	−0.62	−0.72	−0.59
EE	−1.33	−2.04	−2.37	−2.29

[a] For the ZZ conformer (fully optimized and flat) the total MP2 energy (in au) is displayed. The numbers in parentheses include the ZPE contribution. [b] See Section III for explanation. Energies with respect to the fully optimized ZZ conformer. [c] Except for the ZZ conformer all other structures are flat. [d] See Section III for explanation. Energies with respect to the flat optimized ZZ structure.

TABLE 2: Energies (in kcal/mol) of Different Structures of 3-(Difluoromethyl)acroleine Relative to the ZZ Conformer Calculated in the MP2 Approximation with Different Correlation Consistent Basis Sets[a]

	basis set			
conformer	cc-pVDZ	cc-pVTZ	*aug*-cc-pVDZ	*aug*-cc-pVTZ
fully optimized structures				
ZZ	−428.603505	−429.025376	−428.699532	−429.059686
	(−428.537122)	(−428.959087)	(−428.634206)	(−428.993773)
ZE	+0.95	−0.17	−0.26	−0.41
	(+0.82)	(−0.20)	(−0.34)	(−0.43)
EZ	−1.31	−1.40	−1.24	−1.17
	(−1.43)	(−1.52)	(−1.32)	(−1.33)
EE	−2.32	−3.13	−3.30	−3.26
	(−2.51)	(−3.25)	(−3.32)	(−3.36)
fictious structures[b]				
EZ	+0.16	+0.08	+0.21	+0.28
EE	−0.73	−1.21	−1.28	−1.18
flat optimized structure[c]				
ZZ	−428.603505	−429.025327	−428.699430	−429.059497
ZE	+0.95	−0.20	−0.32	−0.52
fictitious flat structures[d]				
EZ	+0.16	+0.02	+0.08	+0.14
EE	−0.73	−1.38	−1.57	−1.56

[a] For the ZZ conformer (fully optimized and flat) the total MP2 energy (in au) is displayed. The numbers in parentheses include the ZPE contribution. [b] See Section III for explanation. Energies with respect to the fully optimized ZZ conformer. [c] Except for the ZZ conformer all other structures are flat. [d] See Section III for explanation. Energies with respect to the flat optimized ZZ structure.

It is also worthwhile to mention that for larger and more flexible basis sets the MP2 calculations with full geometry optimization predict the energy ordering of conformers as EE < EZ < ZE < ZZ. This ordering holds for both 3-methylacroleine and 3-(difluoromethyl)acroleine. The energy differences for different conformers of the two molecules are similar.

In addition to the energy data for fully optimized structures, we have also included the MP2 energies of the constrained "flat" ZZ species with the HC−CH═CH−CH═O skeleton in one plane. In the case of the ZZ conformer most basis sets predict some out-of-plane tilting of the hydrogen atom of the C−H···O(═C) fragment and a very small (negligible) out-of-plane rotation of the aldehyde group. The out-of-plane angle (ϕ) defined as the angle between the C−H bond and the plane of the C═C−C fragment strongly depends on the basis set used in calculations. The corresponding data are summarized in Table 3.

Although the tilt angle for the C−H bond in the fully optimized ZZ structures may assume considerably large values (see Table 3), the energy differences between flat and fully optimized ZZ conformers are usually of the of the order of 10^{-4} au $\approx$ 0.06 kcal/mol (see Table 3). Thus, the fully optimized ZZ conformers with nonzero value of ϕ correspond to one of the two minima on the full potential energy surface separated by a very small barrier (B). The value of B is much lower than the lowest vibrational energy and has no significance for the infrared spectra in the C−H stretch region. However, the nonzero values of ϕ indicate that the hydrogen atom of the C−H

TABLE 3: Out-of-Plane Angle (ϕ, in degrees) between the C−H Bond and the (H_3)C−C═C Plane in the Fully Optimized ZZ Structure and the Barrier to Planarity (B, in kcal/mol) for 3-Methylacroleine and 3-(Difluoromethyl)acroleine

	basis set			
	cc-pVDZ	cc-pVTZ	*aug*-cc-pVDZ	*aug*-cc-pVTZ
	3-methylacroleine			
ϕ	0	9	31	18
B	0.00	0.01	0.07	0.06
	3-(difluoromethyl)acroleine			
ϕ	0	14	15	16
B	0.00	0.03	0.06	0.12

bond is pushed out of the C−H···O region. The meaning of this finding will be discussed (Section V) in the context of the estimates of the energy of the intramolecular C−H···O “hydrogen bond”.

On inspecting the data of Table 3, one finds that the ϕ angle in 3-methylacroleine strongly increases on passing from cc-pVDZ ($\phi = 0°$) to *aug*-cc-pVDZ ($\phi = 31°$) basis set. This increase is most likely caused by adding diffuse functions to the cc-pVDZ basis set that enhance the valence repulsion effect in the C═O···H−C interaction. A much smaller value of ϕ (18°) is obtained with the *aug*-cc-pVTZ basis set. This may suggest that the *aug*-cc-pVDZ basis set is a little unbalanced to be used for calculations of interaction energies.

In the case of 3-(difluoromethyl)acroleine, all basis sets larger than cc-pVDZ uniformly predict the tilt angle of about 15°. The basis set diffuseness becomes less important because of the strong polarization of the C−H bond of the difluoromethyl group. This confirms our interpretation of the origin of the large value of ϕ calculated with the *aug*-cc-pVDZ basis sets in the fully optimized ZZ form of 3-methylacroleine.

One more interesting feature of the ZZ conformer of 3-methylacroleine follows from calculations on the structure with the C−H bond of the CH_3 group tilted by $\phi = 60°$. The MP2/*aug*-cc-pVDZ energy of this structure is a little (by less than 0.01 kcal/mol after including the ZPE correction) lower than that for $\phi = 31°$. The two minima are separated by a negligibly small barrier. Upon combining these data with those for the quasi-planar ZZ conformer, one finds that the CH_3 group almost freely rotates about the C−C bond. However, this free rotation is actually a uniformly hindered rotation (i.e., the potential $V(\phi)$ is almost constant).

For the purpose of the estimation of the energy contribution due to the C−H···O(═C) interaction (i.e., the energy of the intramolecular C−H···O hydrogen bond), we have carried out MP2 calculations for fictitious structures EZ,f and EE,f of the EZ and EE conformers, respectively. These structures have all bond distances and valence angles the same as in the fully optimized ZZ conformer and differ from it by the rotation either about the CC double bond (EZ,f) or about both the single and double CC bonds (EE,f). These data will be used to estimate the energy contribution due to the C−H···O(═C) contact in the ZZ conformer (see Section IV) according to methods proposed recently by us.[30] These methods[30] have been found to give reasonable energy estimates for traditional intramolecular bonds, and it is interesting to apply them in the present case of presumably weak interactions due to the C═O···H−C contact.

The data of Tables 1 and 2 include also the energy values (in parentheses) corrected for the so-called zero-point (vibration) energy (zpe). The zpe-corrected total energy of the fully optimized ZZ conformer and the corresponding relative energies of the other three fully optimized conformers are shown. Formally, the zpe contribution is defined in terms of the frequency data for fully optimized structures. However, if the deviation from the minimum energy structure is small, one can use the same value of zpe for non-optimized structures. Hence, the same value of the zpe correction will be assumed (Section V) for fully optimized and constrained (flat or fictitious) structures.

To complete this section, let us also remark about the basis set dependence of the present data. With respect to the evaluation of the relative energy of different conformers the cc-pVTZ and both augmented basis sets give, in most cases, comparable results. However, the relative energy values obtained with the smallest cc-pVDZ are much less reliable and may lead to incorrect energy ordering of different conformers. We have also carried out some selected calculations with cc-pVQZ (4ζ) basis sets. For the EE conformer of 3-methylacroleine, its MP2 energy calculated with cc-pVQZ basis set is by 3.85 kcal/mol lower than that of the fully optimized ZZ conformer. The out-of-plane ϕ angle in the ZZ conformer is found to be 17°. Both these results are very close to those calculated with *aug*-cc-pVTZ basis set (see Tables 1 and 3). The corresponding data for the EE conformer of 3-(difluoromethyl)acroleine, 3.31 kcal/mol and 16°, respectively, show the same regularity. This indicates that the MP2 results obtained with the largest *aug*-cc-pVTZ should be sufficiently well converged with respect to the basis set extension. Hence, when discussing the frequency data and the estimated interaction energies due to the C−H···O(═C) contact most attention will be given to the results evaluated with the *aug*-cc-pVTZ basis set.

IV. C−H Stretching Frequency and Bond Distance

The C−H stretching frequency (ν_{CH}) and C−H bond distance (r_{CH}) data for the ZZ conformer of 3-methylacroleine are presented in Table 4 and accompanied by differences with respect to the other three conformers. For the given conformer C, the listed values correspond to differences evaluated as

$$\Delta\nu_{CH}(ZZ,C) = \nu_{CH}(ZZ) - \nu_{CH}(C) \qquad (1)$$

and

$$\Delta r_{CH}(ZZ,C) = r_{CH}(ZZ) - r_{CH}(C) \qquad (2)$$

Thus, the positive value of $\Delta\nu_{CH}(ZZ,C)$ means that the C−H stretching frequency in the conformer ZZ is blue-shifted with respect to the conformer C. Similarly, the negative value of $\Delta r_{CH}(ZZ,C)$ shows that the C−H bond in the ZZ conformer is shorter than the relevant bond in the conformer C. The same set of data for 3-(difluoromethyl)acroleine is presented in Table 5.

Most of the data of Tables 4 and 5 show that the ZZ conformer exhibits the highest C−H stretching frequency and the shortest value of the r_{CH} distance of the C−H bond involved in interaction with oxygen of the aldehyde group. Certain irregularity observed in the results for 3-methylacroleine calculated with the *aug*-cc-pVDZ basis set is presumably of the same origin as that discussed earlier in the context of the out-of-plane tilt angle ϕ. Upon imposing the planarity constraint on the ZZ structure there is in general a marked increase of the calculated C−H stretching frequency. For the *aug*-cc-pVTZ basis set this increase amounts to about $+20$ cm^{-1} for both 3-methylacroleine and 3-(difluoromethyl)acroleine. Only for the small cc-pVDZ basis set do MP2 calculations predict the ZZ structure to be planar. The r_{CH} data for the conformer ZZ and the $\Delta r_{CH}(ZZ,C)$ values with respect to the other three conformers

TABLE 4: Harmonic C−H Stretching Frequency (ν_{CH}, in cm^{-1}) and C−H Bond Distance (r_{CH}, in Å) in Fully Optimized Form of the ZZ Conformer of 3-Methylacroleine and the Corresponding Frequency ($\Delta\nu_{CH}$) and Bond Distance (Δr_{CH}) Differences for Other Fully Optimized Conformers of 3-Methylacroleine from MP2 Calculations with Correlation Consistent Basis Sets[a]

		basis set			
conformer		cc-pVDZ	cc-pVTZ	*aug*-cc-pVDZ	*aug*-cc-pVTZ
ZZ	ν_{CH}	3232	3205	3161	3181
		(3232)	(3210)	(3199)	(3200)
	r_{CH}	1.0959	1.0831	1.0982	1.0852
		(1.0958)	(1.0827)	(1.0951)	(1.0837)
ZE	$\Delta\nu_{CH}{}^{b}$	+33	+19	−13	+2
		(+33)	(+25)	(+26)	(+22)
	$\Delta r_{CH}{}^{c}$	−0.0025	−0.0015	+0.0010	−0.0001
		(−0.0026)	(−0.0019)	(−0.0022)	(−0.0017)
EZ	$\Delta\nu_{CH}{}^{a}$	+68	+54	+20	+36
		(+68)	(+59)	(+58)	(+55)
	$\Delta r_{CH}{}^{b}$	−0.0055	−0.0045	−0.0020	−0.0031
		(−0.0056)	(−0.0050)	(−0.0052)	(−0.0046)
EE	$\Delta\nu_{CH}{}^{b}$	+63	+49	+15	+31
		(+63)	(+54)	(+53)	(+50)
	$\Delta r_{CH}{}^{c}$	−0.0052	−0.0042	−0.0017	−0.0028
		(−0.0053)	(−0.0046)	(−0.0048)	(−0.0043)

[a] The numbers in parentheses are for the “flat” form of the ZZ conformer. [b] Shift in ZZ with respect to the conformer C; C = ZE, EZ, EE. See eq 1. [c] Shift in ZZ with respect to the conformer C; C = ZE, EZ, EE. See eq 2.

TABLE 5: Harmonic C−H Stretching Frequency (ν_{CH}, in cm^{-1}) and C−H Bond Distance (r_{CH}, in Å) in Fully Optimized Form of the ZZ Conformer of 3-(Difluoromethyl)acroleine and the Corresponding Frequency ($\Delta\nu_{CH}$) and Bond Distance (Δr_{CH}) Differences for Other Fully Optimized Conformers of 3-(Difluoromethyl)acroleine from MP2 Calculations with Correlation Consistent Basis Sets[a]

		basis set			
conformer		cc-pVDZ	cc-pVTZ	*aug*-cc-pVDZ	*aug*-cc-pVTZ
ZZ	ν_{CH}	3241	3219	3223	3204
		(3241)	(3229)	(3235)	(3222)
	r_{CH}	1.0943	1.0823	1.0941	1.0840
		(1.0943)	(1.0817)	(1.0934)	(1.0827)
ZE	$\Delta\nu_{CH}{}^{b}$	+62	+40	+36	+28
		(+62)	(+50)	(+48)	(+46)
	$\Delta r_{CH}{}^{c}$	−0.0043	−0.0027	+0.0025	−0.0018
		(−0.0043)	(−0.0034)	(−0.0032)	(−0.0032)
EZ	$\Delta\nu_{CH}{}^{b}$	+102	+82	+72	+68
		(+103)	(+92)	(+83)	(+85)
	$\Delta r_{CH}{}^{c}$	−0.0080	−0.0065	−0.0058	−0.0054
		(−0.0080)	(−0.0071)	(−0.0064)	(−0.0067)
EE	$\Delta\nu_{CH}{}^{b}$	+96	+75	+66	+62
		(+96)	(+85)	(+78)	(+80)
	$\Delta r_{CH}{}^{c}$	−0.0076	−0.0061	−0.0054	−0.0051
		(−0.0076)	(−0.0067)	(−0.0061)	(−0.0064)

[a] The numbers in parentheses are for the “flat” form of the ZZ conformer. [b] Shift in ZZ with respect to the conformer C; C = ZE, EZ, EE. See eq 1. [c] Shift in ZZ with respect to the conformer C; C = ZE, EZ, EE. See eq 2.

show essentially the same pattern of the basis set dependence as the frequency data.

It has been already mentioned (Section III) that the CH$_3$ group in the ZZ conformer of 3-methylacroleine experiences only a little (uniform) hindrance with respect to its rotation about the single C−C bond. However, the MP2/*aug*-cc-pVDZ data for $\phi = 60°$ show that the C−H frequency is lowered to 3153 cm^{-1} from its values of 3199 and 3161 cm^{-1} for the planar and optimized out-of-plane structures, respectively. This shows that the valence repulsion effect strongly depends on the variation of the O···H distance. For $\phi = 60°$ this distance becomes equal to 2.64 Å and is longer than the sum (about 2.60 Å) of the van der Waals radii for oxygen and hydrogen.[34] In consequence for $\phi = 60°$ the blue shift with respect to the EE conformer amounts to only +7 cm^{-1} as compared to its values of +53 and +15 cm^{-1} for $\phi = 0°$ (planar) and $\phi = 31°$ (fully optimized), respectively.

For the largest *aug*-cc-pVTZ basis set used in our calculations the data of Tables 4 and 5 show that in the ZZ conformer the C−H···O=C intramolecular interaction leads to the blue shift of the C−H stretching frequency and the decrease of the C−H bond distance irrespectively of the reference conformer. However, to establish representative numerical values of $\Delta\nu_{CH}$(ZZ,C) and Δr_{CH}(ZZ,C) one must refer them to some selected conformer C. The relevant C−H bond in this reference conformer should as much as possible correspond to the fictitious ZZ system without the C−H···O=C interaction. The ZE conformer certainly does not satisfy this requirement since it will exhibit a rather strong interaction between the hydrogens of the two C−H bonds. This is seen from relatively small values of $\Delta\nu_{CH}$(ZZ,ZE) and Δr_{CH}(ZZ,ZE). Hence, the most suitable reference conformers appear to be the EZ and EE forms.

In both EZ and EE conformers the C−H bond in question remains almost free of direct repulsive interactions with other fragments of the two investigated molecules (Figure 1). Moreover, the changes of bond distances and valence angles in the O=C−C=C−C skeleton, which arise upon the conformation change from ZZ to either EZ or EE, are insignificant. Indeed, the $\Delta\nu_{CH}$(ZZ,EZ) (Δr_{CH}(ZZ,EZ)) and $\Delta\nu_{CH}$(ZZ,EE) (Δr_{CH}(ZZ,EE)) evaluated for 3-methylacroleine (Table 4) and

3-(difluoromethyl)acroleine (Table 5) are almost independent of the choice between the two reference conformers. According to the tabulated data our MP2/*aug*-cc-pVTZ calculations for 3-methylacroleine predict that the C−H···O═C contact leads to the blue shift of the C−H stretching frequency by about +30 cm^{-1}. In 3-(difluoromethyl)acroleine this shift can be estimated at the level of about +60 cm^{-1}.

The blue shift of the C−H bond stretching frequency in the ZZ conformer evaluated with respect to EZ and/or EE conformers is consistently followed by the decrease of the C−H bond distance. In 3-methylacroleine this shortening of the C−H bond can be estimated at the level of about −0.003 Å (MP2/*aug*-cc-pVTZ, Table 4). In 3-(difluoromethyl)acroleine the corresponding result is about −0.005 Å.

Both the frequency shift and the change of the C−H bond distance that occur in the ZZ conformer with respect to EZ and EE structures clearly indicate that the C−H···O═C contact brings about the characteristic blue-shifting features. This conclusion is obviously based on the choice of the reference values for the "free" C−H bond. Owing to the richness of conformations of the two investigated molecules, a plausible reference system could have been found and used to unambiguously establish the blue-shifting character of the C−H···O═C intramolecular interaction. Obviously, the numerical estimates of the magnitude of this shift are and will always be uncertain. Although the blue shift can be considered to be well documented, this does not explicitly tell if the interaction is (locally) repulsive or attractive and in this respect it is worthwhile to refer to the calculated data for H···O contact distances in the ZZ conformer.

For 3-methylacroleine (MP2/*aug*-cc-pVTZ data of Table 4) the H···O contact distance in the fully optimized ZZ conformer is found to be equal to 2.31 Å. The cc-pVDZ, cc-pVTZ, and cc-pVQZ basis sets give 2.27, 2.28, and 2.30 Å, respectively. Much larger value (2.39 Å) is obtained with the *aug*-cc-pVDZ set. This is because of the large value of the tilt angle ϕ (see Table 3). One should note that the MP2/*aug*-cc-pVTZ result is much shorter than the sum (≈2.60 Å) of the van der Waals radii for hydrogen (≈1.20 Å) and oxygen (≈1.40 Å).[34] Although the sum of the van der Waals radii may not be the best measure of the mutual repulsion in the C−H···O═C contact, it clearly shows that the local minimum which corresponds to the ZZ structure arises from the balance between energy losses and gains in the whole system.

In the case of the ZZ conformer of 3-(difluoromethyl)acroleine the H···O distance varies between 2.26 Å (MP2/cc-pVDZ) and 2.29 Å (MP2/*aug*-cc-pVTZ) and only marginally depends on the basis set used in calculations. Depending on the basis set the calculated H···O distance in the ZZ conformer of 3-(difluoromethyl)acroleine is either very close to or a little shorter than the corresponding values obtained for 3-methylacroleine. This suggests that in the ZZ conformer of 3-(difluoromethyl)acroleine the H···O contact is also repulsive, although the stronger polarization of the C−H bond in the CHF_2 group enhances the electrostatic attraction with the aldehyde oxygen. The intramolecular interaction makes the C−H bond compressed, and in consequence, leads to the blue shift of its stretching frequency. These features should be reflected by estimates of the energy of intramolecular interactions.

One more indication of the repulsive character of the C−H···O═C interaction follows from the evaluation of the C−H···O angle in fully optimized and constrained ZZ conformers. The C−H···O fragment of the intramolecular interaction between the C−H and O═C groups is definitely nonlinear and the optimized structure is of the chelate (benzene-like) form. In the fully optimized, unconstrained ZZ structure of 3-methylacroleine the C−H···O angle is equal to 118.5° and increases to 125.8° upon the planarity constraint. For 3-(difluoromethyl)acroleine the corresponding data are 116.5° and 122.7°. The increase of the C−H···O angle on passing to the flat structure shows that the intramolecular H···O repulsion increases and is compensated by some expansion of the chelate ring. A part of this repulsion leads to the compression of the C−H bond that becomes shorter than in the fully optimized ZZ conformers (see Tables 4 and 5).

V. Energy Contribution Due to the Intramolecular C−H···O Contact

For both molecules investigated in this paper the chelate-type ZZ structure represents a local minimum on the total energy hypersurface. One may conclude that the possible repulsion between the hydrogen end of the C−H bond and the oxygen atom is not strong enough to force the rotation about the HOC−C single bond which would lead to the ZE conformer. The compression in the C−H···O region has been well-documented by the C−H frequency and bond distance data and the repulsive local interaction is a plausible explanation of the observed effect.

Most chemists would refer to the energy contribution due to certain (presumably bonding) intramolecular interaction as the corresponding *intramolecular bond energy*. The common example of this terminology is reflected in discussions of the intramolecular hydrogen bond.[35] Somehow it does not seem to have been clearly recognized that such a bond in a polyatomic systems, in particular a weak bond, is primarily in the mind of a chemist. There is no method based on rigorous quantum mechanical treatment which would give unambiguous definition of these bonds and their energies. Yet one can try to devise some, say "reasonable", partition schemes that give certain numbers reflecting the magnitude of intramolecular interaction energies. For traditional, red-shifting hydrogen bonds the meaning of reasonable usually anticipates that the estimated energy is of a similar order of magnitude as the energies of intermolecular hydrogen bonds. This reasoning can be further supported by different correlations between intermolecular interaction energies and other features of interacting systems.[28,35−38]

Over the past years different partition schemes have been proposed to estimate the energy of traditional intramolecular hydrogen bonds.[30,39−42] All of them attempt to manipulate total molecular energies to extract the energy difference between that of the H-bonded system and the fictitious structure of the same geometry and with the eliminated H-bond contact interactions. In most cases, however, the reference structures that are used for this purpose have the bond distances and valence angles significantly different from those in the H-bonded system. To take into account this geometry factor we have recently devised an alternative scheme for the estimation of intramolecular H-bond energies.[30] This scheme (scheme A of ref 30) appears to be particularly suitable for the estimation of the energy contribution due to C−H···O contact in 3-methylacroleine and 3-(difluoromethyl)acroleine and will be employed in the present study.

According to the estimation scheme A of ref 30 the geometry factor is taken into account by considering fictitious conformers (EZ,f) and (EE,f), which correspond to the same values of bond distances and valence angles as in the ZZ conformer. Then, the estimate of the intramolecular hydrogen bond energy, E_{HB}^{A}, can be written as:[30]

$$E_{\mathrm{HB}}^{\mathrm{A}} = \frac{1}{2}(E^{\mathrm{EZ,f}} + E^{\mathrm{EE,f}}) - E^{\mathrm{ZZ}} \qquad (3)$$

If the changes in zpe are taken into account, then the corresponding estimate of the H-bond energy, $E_{\mathrm{HB,zpe}}^{\mathrm{A}}$, becomes:

$$E_{\mathrm{HB,zpe}}^{\mathrm{A}} = E_{\mathrm{HB}}^{\mathrm{A}} + \Delta_{\mathrm{zpe}}^{\mathrm{A}} \qquad (4)$$

where $\Delta_{\mathrm{zpe}}^{\mathrm{A}}$ is defined in terms of the corresponding zpe corrections for EZ, EE, and ZZ structures:

$$\Delta_{\mathrm{zpe}}^{\mathrm{A}} = \frac{1}{2}(\Delta E_{\mathrm{zpe}}^{\mathrm{EZ}} + \Delta E_{\mathrm{zpe}}^{\mathrm{EE}}) - \Delta E_{\mathrm{zpe}}^{\mathrm{ZZ}} \qquad (5)$$

where $\Delta E_{\mathrm{zpe}}^{\mathrm{C}}$ denotes the zpe correction to the energy of the conformer C. Note that $\Delta_{\mathrm{zpe}}^{\mathrm{A}}$ is evaluated from the data for fully optimized structures. Thus, it should be considered as an approximation to the correction, which cannot be defined for nonoptimized structures.

Although eq 3 has been suggested[30] for the estimation of the energy of traditional red-shifting intramolecular hydrogen bonds, there should be no formal objection to use it also in the present case. Moreover, one may expect it to work even better than in the case of strong intermolecular hydrogen bonds investigated in our earlier paper.[30] In the present case, the difference between fully optimized and fictitious structures is relatively small, and the contribution of the geometry factor is less important.

In addition to the estimation method based on eq 3 we have also considered[30] a very simple (and crude) scheme (scheme B) that follows from the consideration of the ZZ → ZE transition. This leads to another estimate, $E_{\mathrm{HB}}^{\mathrm{B}}$, of the intramolecular hydrogen bond energy:

$$E_{\mathrm{HB}}^{\mathrm{B}} = E^{\mathrm{ZE}} - E^{\mathrm{ZZ}} \qquad (6)$$

whose applicability will be investigated in the present study of the energy contributed by the intramolecular C−H···O contact. The zpe-corrected counterpart of eq 6 is given by

$$E_{\mathrm{HB,zpe}}^{\mathrm{B}} = E_{\mathrm{HB}}^{\mathrm{B}} + \Delta_{\mathrm{zpe}}^{\mathrm{B}} \qquad (7)$$

where

$$\Delta_{\mathrm{zpe}}^{\mathrm{B}} = \Delta E_{\mathrm{zpe}}^{\mathrm{ZE}} - \Delta E_{\mathrm{zpe}}^{\mathrm{ZZ}} \qquad (8)$$

One should note that according to definitions in eqs 3, 4, 6, and 7 the positive values of these intramolecular interaction energies correspond to the formation of the (attractive) hydrogen bond.

The simple estimation scheme B is obviously much less reliable than scheme A since it includes the repulsive contribution due to the interaction between hydrogens of the two C−H bonds facing each other in the ZE conformer. On the other hand, it requires only two energy values, and it appears to be worthwhile to check its performance and the possibility of its use in straightforward estimations of the energy of intramolecular contacts or bonds.

Both $E_{\mathrm{HB}}^{\mathrm{A}}$ and $E_{\mathrm{HB}}^{\mathrm{B}}$ and their zpe-corrected counterparts can be evaluated with the aid of the energy data presented in Tables 1 and 2. The results are shown in Table 6. Additionally this table includes also the A and B estimates of the intramolecular interaction energy due to the C−H···O contact for the flat form of the ZZ conformer.

The results obtained with the cc-pVDZ basis set significantly differ from the other data presented in Table 6. All larger and more flexible basis sets predict a *negative* energy contribution due the C−H···O contact in both 3-methylacroleine and 3-(difluoromethyl)acroleine. If the intramolecular C−H···O interaction were recognized as the intramolecular hydrogen bond, the negative values of the associated hydrogen bond energy would lead to the conclusion that this interaction actually corresponds to what one would call the repulsive contact or the "hydrogen anti-bond". As calculated from the two estimation schemes, the C−H···O region in the ZZ conformer is weakly repulsive.

TABLE 6: Estimates of the Energy Contribution (in kcal/mol) Due to the C−H···O Contact in 3-Methylacroleine and 3-(Difluoromethyl)acroleine

	basis set			
estimate[a]	cc-pVDZ	cc-pVTZ	*aug*-cc-pVDZ	*aug*-cc-pVTZ
3-methylacroleine, fully optimized ZZ conformer				
E_{HB}^{A}	−0.88	−1.20	−0.84	−1.01
$E_{\mathrm{HB,zpe}}^{A}$	−0.99	−1.21	−0.75	−1.03
E_{HB}^{B}	+0.13	−0.83	−1.06	−1.18
$E_{\mathrm{HB,zpe}}^{B}$	+0.06	−0.76	−0.99	−1.09
3-methylacroleine, flat optimized ZZ conformer				
E_{HB}^{A}	−0.88	−1.33	−1.55	−1.44
$E_{\mathrm{HB,zpe}}^{A}$	−0.99	−1.34	−1.46	−1.46
E_{HB}^{B}	+0.13	−0.84	−1.13	−1.24
$E_{\mathrm{HB,zpe}}^{B}$	+0.06	−0.77	−1.06	−1.15
3-(difluoromethyl)acroleine, fully optimized ZZ conformer				
E_{HB}^{A}	−0.28	−0.57	−0.54	−0.45
$E_{\mathrm{HB,zpe}}^{A}$	−0.43	−0.69	−0.59	−0.58
E_{HB}^{B}	+0.95	−0.17	−0.26	−0.41
$E_{\mathrm{HB,zpe}}^{B}$	+0.82	−0.20	−0.34	−0.43
3-(difluoromethyl)acroleine, flat optimized ZZ conformer				
E_{HB}^{A}	−0.28	−0.68	−0.75	−0.71
$E_{\mathrm{HB,zpe}}^{A}$	−0.43	−0.80	−0.80	−0.84
E_{HB}^{B}	+0.95	−0.20	−0.32	−0.52
$E_{\mathrm{HB,zpe}}^{B}$	+0.82	−0.23	−0.40	−0.54

[a] For the estimation scheme A, see eqs 3 and 4. The energies for the estimation scheme B are defined by eqs 6 and 7.

The data for the flat ZZ structure show some increase of the repulsion and confirm our earlier conclusions concerning the origin of the blue shift in the C−H stretching frequency and the shortening of the C−H bond distance. Once the ZZ structure is forced to assume the flat form, the hydrogen atom of the C−H bond must feel a stronger valence repulsion. This effect is diminished in 3-(difluoromethyl)acroleine because of the increase of the attractive electrostatic component of the intramolecular interaction energy.

Although the C−H···O interaction is found to be weakly repulsive the chelate-like ZZ structure is a stable local minimum on the molecular energy hypersurface. This leads to a quite deceptive structure which may suggest the presence of the true intramolecular hydrogen bond. The estimates of the energy contribution due to this bond reveal that no hydrogen bonding is involved.

Obviously, our conclusion that the C−H···O region is actually repulsive relies on the methods for the estimation of the corresponding contribution to the total molecular energy. These methods, as discussed in our recent paper,[30] depend on a rather arbitrary definition of the energy contributed by some structural unit. For traditional red-shifting hydrogen bonds different definitions[30] may lead to significantly different estimates. The present results of the two estimation schemes should be understood mostly in a qualitative way. They do not eliminate the possibility that some other schemes[30,39−42] may give small positive values of the contribution due to the intramolecular C−H···O contact. Thus, if there is any hydrogen bonding involved it must be very weak.

At the first sight, the present estimates of the energy contributed by the C−H···O contact seem to contradict the results of the recent study of the 4-*N*,*N*-dimethylamino-1,1,1-trifluoro-3-buten-2-one dimer.[46] In this case a blue shift of the H−C═ frequency has been found and associated with the interaction of the H−C═ group in one of the two molecules with the C═O group of the other. By using the NMR data the authors obtained the dimerization enthalpy and then estimated the energy contribution by each of the two pairs of intermolecular contacts. In the present convention of sign this contribution is positive and amounts to about +3 kcal/mol. However, this estimation is based on the assumption that all of the dimerization energy is due to C−H···O contacts. On the other hand, the monomer molecule has a large dipole moment (about 7.5 D) and the dimer structure should primarily arise from the strong dipole−dipole interaction. The resulting force compresses the dimer and leads to the compression of the H−C═ bond accompanied by the blue-shift of its stretching frequency. This alternative interpretation shows again that to define the energy contribution due to particular intramolecular (or intermonomer) interaction is quite ambiguous.

The negative energy contributions due to the C−H···O intramolecular interaction nicely confirm the results already discussed in Sections III and IV. Upon associating the blue-shift of the C−H stretching frequency with the valence repulsion[12] between the two fragments of the ZZ conformer one finds that the C−H bond in the chelate-structure must be significantly compressed. This leads to the decrease of the C−H bond distance and increase of the C−H stretching force constant and is supported by the energy data of Table 6.

VI. Summary and Conclusions

The effect of the intramolecular C−H···O contact has been investigated for 3-methylacroleine and 3-(difluoromethyl)-acroleine in the ZZ conformation. The MP2 energy data show that the ZZ conformers of both molecules correspond to local minima on the total energy hypersurface that are well-separated from the other minima by high enough barriers to the internal rotation about HOC−C and C═C bonds. This leads to the intramolecular compression of the C−H bond and is reflected in other features of the investigated molecules.

Because of the existence of several stable conformers, the two model systems considered in this paper offer a rather unique possibility of finding the appropriate reference conformation which approximately corresponds to the situation of the CH_3 group in the fictitious ZZ structure with the removed C−H···O interaction. Both EZ and EE conformers are found to be suitable for this purpose and used to establish the direction of the C−H stretching frequency shift and the change in the C−H bond distance. In this way the C−H···O contact in ZZ conformers of 3-methylacroleine and 3-(difluoromethyl)acroleine is proven to result in the blue shift of the C−H stretching frequency. This shift is paralleled by the shortening of the C−H bond distance.

Having established that the intramolecular C−H···O interaction in the two studied molecules has the blue-shifting character, we have estimated the energy contribution due to this contact. The two estimates considered in this paper lead to the conclusion that the C−H···O interaction is repulsive. Hence, one should refer to it by the term C−H···O *contact* rather than to call it the intramolecular hydrogen *bond*, although the formal structure of the ZZ conformer would suggest it otherwise.

The blue-shifting character of some intramolecular interactions has been recently considered by Li et al.[12] and Fang et al.[27] and appears to be a rather common feature of sterically compressed systems. Actually, the first observation of the blue-shift of the C−H stretching frequency due to C−H···O intramolecular interactions goes most likely to the 1955−1963 papers by Pinchas,[23−26] although this has not been recognized by this author. The major problem in establishing (relatively small) blue shifts of the C−H stretching frequency is to find the right reference system that is likely to simulate the C−H bond in the presence of the lone pair donor although without their mutual interaction. The present data show that a simple rotation of the aldehyde group does not provide the appropriate reference for the C−H bond interaction with the aldehyde oxygen. Using such a reference may not give unambiguous answers concerning the blue- or red-shifting features of the intramolecular interaction.

The results of our calculations are uniformly interpreted in terms of the intramolecular compression or valence repulsion between two molecular fragments. This repulsion significantly depends on the mutual distance between these fragments that can be modified by the confinement[43−45] or, for example, external pressure. In particular, the pressure effects, which are essentially due to valence repulsion between the given molecule and its surrounding, can be easily modeled[43] and were found to significantly increase the blue-shifting character of weak intramolecular interactions.

References and Notes

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