An INDO Investigation of the Structure and Bonding of Acetylacetone and Trifluoroacetylacetone

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Abstract: The energies of the enol forms of acetylacetone (ACAC) and trifluoroacetylacetone (TFA) have been minimized with respect to all structural parameters using the INDO molecular orbital theory. The internal hydrogen for enol ACAC is found to be symmetrically arranged between the two oxygens with an OHO angle of 152° and an OH bond length of 1.174 Å. Fluorine substitution to produce the electronically asymmetric molecule TFA causes only a slight asymmetry in the position of the internally bonded hydrogen. In both molecules this hydrogen is located in a well-defined single potential energy minimum. Electron density is increased on the carbon α to the CF_3 group in TFA relative to ACAC, while all other ring atoms lose electron density. CF_3 substitution results in an alternation of bond lengths and bond energies about the ring: the α-CC bond is strengthened, the adjacent CO bond weakened, and the OH bond strengthened relative to ACAC with just the opposite effect on the methyl side. Localized orbitals of ACAC indicate the presence of a three-center π bond on the carbon backbone of the enol ring and considerable delocalization of the oxygen lone pairs into the CO bonding region. The results are discussed in light of their implications for building models for interpretation of spectral data and the nature of hydrogen bonding.

The wide variety of molecules in the general class of β-diketones, and their extensive use as chelating ligands for many metals, has served to create considerable interest in the development of accurate descriptions of the geometric configurations of these molecules.[1] The most common β-diketone, acetylacetone (ACAC), is known to exist in at least two tautomeric forms, keto and enol. It is generally accepted that at moderate temperatures the enol form predominates in both gas and liquid phases,[2,3] and in the present work we will concern ourselves exclusively with the enol structure.

Direct physical determinations of the structure of acetylacetone have been few. Lowrey, George, D'Antonio, and Karle[2] examined the gas phase electron diffraction pattern and concluded that the hydrogen bond in the enol is part of a planar ring. They further indicate that the assumption of a linear, symmetric internal hydrogen bond provides a better fit with their radial distribution curve than does an asymmetric disposition of the hydrogen. These results support those obtained by Schaefer and Wheatley[4] on crystalline tetraacetylethane, the dimer of the enol form of acetylacetone. This X-ray diffraction study also suggested that the internally bonded hydrogen was symmetrically placed in a planar ring. While an X-ray determination of the crystal structure of dibenzoylmethane[5] led to the conclusion that the internally bound hydrogen is nonlinear and asymmetric, it is to be noted that this molecule as a whole is nonplanar.

In view of these results, it is curious that every case that we could find, in which the structure of acetylacetone was *modeled* for interpretation of experimental observations, a planar enol ring, with an *asymmetric*, nonlinear hydrogen bond, was chosen. For example, Ogoshi and Nakamoto[6] assume this configuration for the purpose of obtaining a normal coordinate analysis of acetylacetone. Further, most recent molecular orbital calculations on this and similar molecules have *assumed* the asymmetric structure.[7,8] One exception to this is the CNDO/2[9] calculation on the malondialdehyde analog of acetylacetone by Schuster.[10] This author concluded that the internal hydrogen is asymmetrically bound with a very low (0.5 kcal/mol) energy barrier separating the two equivalent minima; however, the coordinates of all atoms except the internal hydrogen were held fixed in *symmetric* positions and the methyl groups of acetylacetone were replaced by hydrogens. Morokuma and coworkers,[8] using the extended Hückel method,[11] concluded that the symmetric structure is very unstable; however, here again no attempt was made to optimize any angles or bond lengths.

Clearly, the geometry of acetylacetone has not been unequivocally established. Most experimental evidence points to a symmetric structure, while most theoretical investigations have assumed an asymmetric structure, and no complete geometry optimization has been carried out. The present work constitutes an attempt to shed some light on this controversy by optimizing the energy of the enol form of acetylacetone with respect to all geometric parameters within the framework of the semiempirical INDO molecular orbital (MO) theory.[12] INDO has been shown to yield reasonable geometries[13] and internal rotation bar-

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(2) A. H. Lowrey, C. George, P. D'Antonio, and J. Karle, *J. Amer. Chem. Soc.*, 93, 6399 (1971).

(3) (a) R. M. Silverstein and G. C. Clayton,"Spectrometric Identification of Organic Compounds," Wiley, New York, N. Y., 1967, p 88; (b) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart and Winston, New York, N. Y., 1969, p 377.

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(13) M. S. Gordon and J. A. Pople, *ibid.*, 49, 4643 (1968).

Table I. INDO Geometries for ACAC and TFA[a]

	Bond lengths					Angles					
	ACAC	TFA		ACAC	TFA		ACAC	TFA		ACAC	TFA
R_{12}	1.395	1.409	R_{78}	1.120	1.120	123	116.82	116.95	178	112.71	113.70
R_{23}	1.395	1.380	R_{79}	1.121	1.123	214	119.47	117.34	179	110.83	107.16
R_{14}	1.324	1.316	$R_{7,10}$	1.121	1.120	235	119.47	121.62	978	107.63	107.14
R_{35}	1.324	1.327	$R_{2,11}$	1.115	1.115	146	106.02	107.96	3,12,13	112.71	116.93
R_{46}	1.174	1.186	$R_{12,13}$	1.120	1.351	356	106.02	103.95	3,12,14	110.83	112.21
R_{56}	1.174	1.167	$R_{12,14}$	1.121	1.353	465	152.18	152.17	13,12,14	107.63	104.67
R_{17}	1.459	1.453	$R_{12,15}$	1.121	1.353	217	124.17	125.47	12,11	121.59	121.52
$R_{3,12}$	1.459	1.472	R_{45}	2.279	2.284	23,12	124.17	120.48	32,11	121.59	121.52

[a] Bond lengths in ångstroms, angles in degrees. See Figure 3 for numbering system.

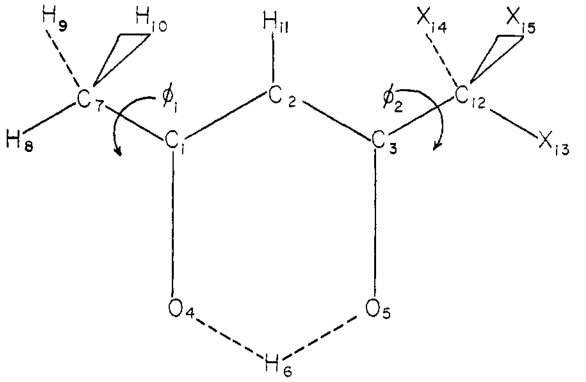

Figure 1. A schematic representation of acetylacetone (X = H) and trifluoroacetylacetone (X = F). ϕ_1 (ϕ_2) is the angle of rotation of the CH_3 (CX_3) group about the CC bond. ϕ_1 (ϕ_2) = 0° when H_8 (X_{13}) eclipses the CO bond.

riers[14-18] for a wide variety of molecules and is generally superior to the less sophisticated CNDO/2 method. Moreover, in view of previous structure analyses[14-18] it was felt that the localized molecular orbitals (LMO's)[19] of acetylacetone would provide some interesting information concerning the bonding in this molecule, and it has been shown[20] that INDO LMO's are generally reliable while those of CNDO are not.

In addition to acetylacetone, we have also carried out geometry optimizations of trifluoroacetylacetone (TFA) in order to determine the effect of an asymmetric substitution on the position of the internal hydrogen and the structure of the ring.

I. Geometries

The structures of acetylacetone and trifluoroacetylacetone are represented schematically in Figure 1. For both molecules the starting geometry was chosen to be the planar, asymmetric structure with $\phi_1 = \phi_2 = 0°$. In the case of the trifluoro-substituted species, the internally bound hydrogen H_6 was initially assumed to be bonded to O_4 (that is, on the methyl side) with a bond length of about 1.03 Å. All $3N - 6$ independent bond lengths, bond angles, and dihedral angles were then allowed to vary with initial (maximum) step sizes of 0.01 (0.10) Å and 0.10 (1.0)°, respectively. The minimization was carried out using a modification of Powell's conjugate directions program,[21] the geometric parameters being organized into sets of no more than nine parameters. All such sets were subjected to the search procedure twice.

The initial geometry minimization of acetylacetone yielded a planar, symmetric ring, with $\phi_1 = \phi_2 = 0°$ and H_6 equidistant between the two oxygens. To check the relative stability of different methyl orientations, the energy was calculated for $\phi_1 = 0°$, $\phi_2 = 180°$, and $\phi_1 = \phi_2 = 180°$, all other geometric parameters being held at their original optimal values. It was discovered that both of the latter geometries were more stable than $\phi_1 = \phi_2 = 0°$ by 0.22 and 0.43 kcal/mol, respectively. The geometry of the latter structure was then reoptimized; however, those parameters external to the ring were assumed to be the same as for the $\phi_1 = \phi_2 = 0°$ structure. Reoptimization of the ring geometry only improved the energy by an additional 0.1 kcal/mol.

The final geometry of acetylacetone is listed in Table I, and clearly INDO predicts a planar, symmetric ring with both methyl groups eclipsing C_2. This is rather different from Schuster's[10] CNDO results, and we can only conclude that a combination of neglecting the methyl groups and using an assumed, fixed geometry by Schuster is the cause of this disparity.

The OHO angle, while not linear as predicted on experimental grounds, is a rather large 152°. It is also interesting to note that the ring CC bond length is nearly identical with the average INDO calculated bond lengths in similar isolated molecules.[22] The same is true for the CO bond length.[22] Thus, according to these results, those infrared absorptions commonly assigned to distinct C=O and C—O stretches (or C=C and C—C) in this molecule actually must be due to normal modes with mixed functional contributions.

To determine the possibility of a stable asymmetric geometry and to investigate the degree to which distortion of the enol ring from the symmetric geometry is

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(14) W. England and M. S. Gordon, *J. Amer. Chem. Soc.*, **93**, 4649 (1971).

(15) W. England and M. S. Gordon, *ibid.*, **94**, 4818 (1972).

(16) M. S. Gordon and W. England, *Chem. Phys. Lett.*, **15**, 59 (1972).

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(18) M. S. Gordon and D. E. Tallman, *Chem. Phys. Lett.*, **17**, 385 (1972).

(19) C. Edmiston and K. Ruedenberg, *Rev. Mod. Phys.*, **35**, 457 (1963).

(20) W. England and M. S. Gordon, *J. Amer. Chem. Soc.*, **91**, 6864 (1969).

(21) M. J. D. Powell, Quantum Chemistry Program Exchange, Program No. 60.

(22) For the purpose of this comparison the molecules most closely related to the CC bond length in ACAC are propane and propene, since the CC bond has an adjacent methyl group in all three cases. The INDO calculated bond lengths for propane (unpublished results) and propene (ref 17) are 1.468 and 1.323 Å, respectively. Similarly, the CO bond lengths predicted by INDO for ethanol (unpublished results) and acetaldehyde (ref 17) are 1.378 and 1.263 Å, respectively. One could choose ethane, ethylene, methanol, and formaldehyde instead. In this case both averages would be lowered by 0.01 Å.

resisted, the O_4–H_6 distance was varied from its equilibrium value of 1.174 to 1.025 Å, the latter value being less than the equilibrium OH bond length predicted by INDO for methanol.[17] The COH angle was reoptimized for each OH distance; however, the remainder of the geometry was held fixed due to computer time considerations. The results of this series of calculations are plotted in Figure 2, and it is clear that any significant distortion of the enol ring from the symmetric geometry is obtained at the expense of a considerable energy loss. For example, when R_{OH} = 1.07 Å (R_{O_6H} = 1.27 Å) the energy is 4 kcal/mol above that of the equilibrium geometry. This corresponds to the degree of distortion ΔR

$$\Delta R = R_{O_6H} - R_{O_4H} \qquad (1)$$

predicted as the equilibrium structure by Schuster.[10] While complete reoptimization of the molecular geometry for each value of R_{OH} might result in a slight flattening of the curve, it is unlikely that the above conclusions would be significantly altered.

The equilibrium bond lengths and angles obtained for trifluoroacetylacetone are also listed in Table I. For this molecule, it was found that a completely planar ring is not the most stable form; however, all ring dihedral angles deviated from planarity by less than 1°, and forcing the ring into a planar geometry only raised the energy by about 0.01 kcal. As for acetylacetone, it was initially assumed that $\phi_1 = \phi_2 = 0°$; however, in contrast to the latter molecule, this was not found to be a stable structure. While ϕ_2 remained $\sim$0°, ϕ_1 = 28.7°. That is, the methyl group is rotated approximately halfway between a structure with one of the hydrogens eclipsing O_4 and a structure with one of the hydrogens eclipsing C_2. Rotation of the CF_3 group by 180° raises the energy (by 0.55 kcal/mol) as does setting ϕ_1 = 60° (by 0.48 kcal/mol); thus, no further geometry search was carried out. It should be noted, however, that for both molecules considered in this paper, we did not carry out a thorough search for other stable geometries with a ring strongly distorted from planarity. Thus, while we can conclude that INDO predicts a stable planar ring for acetylacetone and a stable, nearly planar ring for the trifluoro analog, we cannot unequivocally say that no stable nonplanar geometry exists for either molecule. Experimental evidence[2,4] does, however, imply the latter result for acetylacetone.

Reference to Table I shows that while the enol ring in trifluoroacetone is asymmetric as expected, the distortion from a completely symmetric geometry is small; for example, ΔR_{OH} (see eq 1) is only 0.02 Å. In fact, the ring geometry of the two molecules is strikingly similar, and it is especially interesting that the average values of those bond lengths and angles which are identical in acetylacetone are nearly the same as those predicted for acetylacetone. For example, the average OH distance is 1.176 Å in TFA while R_{OH} = 1.174 Å in ACAC, and the OHO and CCC angles are virtually identical in the two molecules.

More interesting than the degree of asymmetry introduced by CF_3 substitution is the fact that its effect on the bond lengths in the molecule seems to alternate from the point of substitution. Thus the $C(X_3)$—C bond length is larger when X = F, while the adjacent ring CC bond is shorter. Similarly, the ring CC bond on the methyl side lengthens while the corresponding CO bond is shorter. Finally, the ring hydrogen has shifted closer to the CF_3 side of the molecule. These results contradict the argument presented by Ogoshi and Nakamoto[6] on the basis of their normal coordinate analysis of acetylacetone and hexafluoroacetylacetone. These authors propose an inductive mechanism which strengthens the "carbonyl" bond α to CF_3 and weakens the adjacent CC bond, while, by implication, resulting in the internal hydrogen moving toward the methyl. Once again, however, we emphasize that the normal coordinate analyses implicitly assume the existence of distinct single and double CC and CO bonds. Even if this were not the case, however, the inductive argument is a shaky one. According to this, the presence of the CF_3 group induces a positive charge on the α carbon, while in fact CF_3 has been categorized as a $-I^-$ substituent[23] which induces a net *negative* charge on the α carbon, relative to the unsubstituted parent.

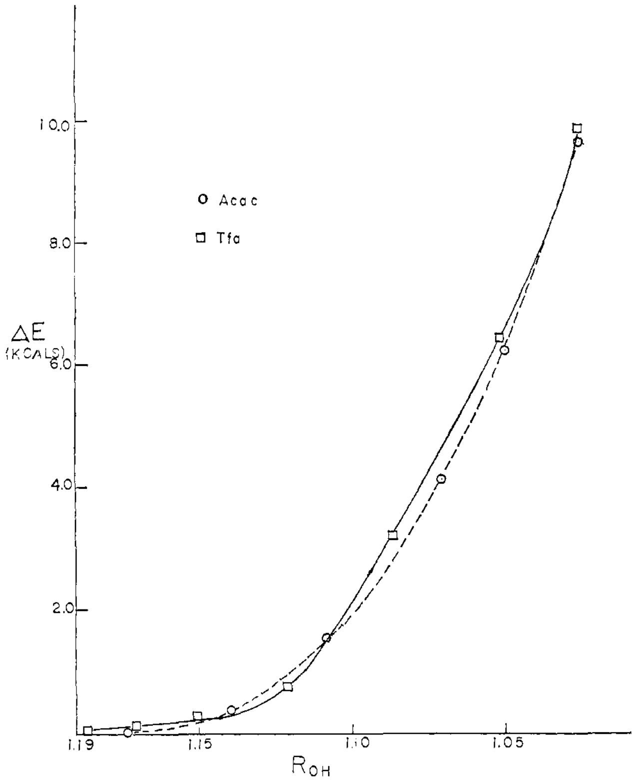

Figure 2. Total energy relative to the equilibrium geometry as a function of O_4–H_6 bond length.

A test of the energy dependence on R_{O_4H} was also carried out on TFA, and the results are plotted in Figure 2. The curve is nearly coincident with that obtained for acetylacetone, and no second minimum exists with H_6 on the methyl side.

II. Electron Densities and Relative Bond Strengths

The electron densities on the atoms of these two molecules are displayed in Figure 3. The large negative charge on the central carbon (C_2) in both molecules is consistent with the charge alternation effect predicted by Pople and Gordon[23] due to back donation from the oxygens. This is diminished somewhat in TFA as ex-

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[23] J. A. Pople and M. S. Gordon, *J. Amer. Chem. Soc.*, **89**, 4253 (1967).

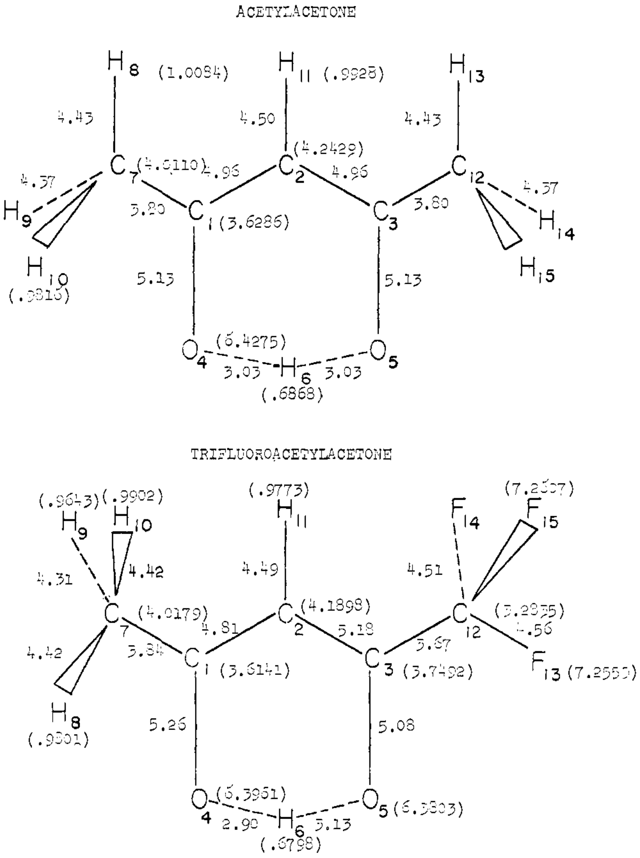

Figure 3. Atomic electron densities (in parentheses) and bond energies (in eV).

pected. Also, as noted in the previous section, CF_3 substitution results in an increase in charge density at the α carbon. All other ring atoms diminish in charge density in TFA, the effect getting smaller with increasing distance from the point of substitution. The predicted dipole moments are 3.65 and 4.75 D for ACAC and TFA, respectively.

Also shown in Figure 3 are the calculated bond energies. These are obtained from the calculated total interference energies[14,24] as described previously.[18] Letting D^e_{XY} be the experimental bond energy for the bond XY in a standard reference molecule[25] and $-\beta_{XY}$ the negative of the total interference energy between XY in the same (geometry-optimized) molecule, we define the normalization factor for the same type of bond in any molecule as

$$N_{XY} = -\beta_{XY}/D^e_{XY} \qquad (2)$$

The calculated bond energy for the bond XY is then taken to be

$$D^c_{XY} = -\beta_{XY}/N_{XY} \qquad (3)$$

where the superscript c indicates a calculated bond energy. Since single and double bonds have different normalization factors, and since the CC and CO bonds of the enol ring really fall into neither of these categories, N for these bonds is taken to be the average of single and double bond normalization factors. On this basis, a CC bond whose strength is halfway between that of ethane and ethylene is expected to have a bond energy of 5.44 eV, while a CO bond whose strength is halfway between that of methanol and formaldehyde should have a bond energy of 5.77 eV. This assumes a linear relationship between the bond energy and the normalization factor and is admittedly rather crude; however, our main interest here is a comparison of the two molecules in question, so the choice of a normalization factor should not be too crucial.

Comparison of Table I and Figure 3 indicates an increase in bond length on going from ACAC to TFA is accompanied by a decrease in bond energy. The converse is also true. As expected, the CC bond on the CF_3 side is strengthened while that on the CH_3 side is weakened by about the same amount. In this regard, it is to be noted that arguments concerning bond energies based on the inductive effect in which an increase in bond strength is correlated with an increase in charge separation in the bond is clearly not followed here. Both ring CC bonds undergo a decrease in charge separation on CF_3 substitution.

The CO bond on the *methyl* side is strongest in TFA, while that on the CF_3 side undergoes a much smaller change (as does the corresponding bond length). Similarly, the $C–CF_3$ bond is weakened by a factor of 3 greater than the $C–CH_3$ bond is strengthened.

The internally bonded hydrogen shifts toward the CF_3 side of the molecule as previously noted and is therefore more strongly bound to the corresponding oxygen; however, the sum of the two OH bond energies is virtually the same in the two molecules. This again is contrary to the speculation by Ogoshi and Nakamoto[6] that the sum will be greater in acetylacetone. Further, the energies of these bonds are much larger than typical intermolecular O—H hydrogen bonds[26] and the corresponding bond lengths much shorter.

III. Localized Orbitals of Acetylacetone

The energy-localized molecular orbitals[19] (LMO's) of acetylacetone are listed in Table II. In the interest of brevity, only those orbitals involving bonds or lone pairs in the ring are included, and these have been truncated so that the tails on the extra-ring atoms have not been included. The latter are similar to the tails in hydrocarbon CH bonds detailed previously.[27] Unfortunately, computer core restrictions prohibit calculation of the LMO's of TFA at the present time.

Due to the symmetry of the enol ring, there are only five distinct localized orbitals: two equivalent CC σ bonds (λ_1), two equivalent CO σ bonds (λ_2), two equivalent OH bonds (λ_3), a three-center CCC π bond (λ_4), and four equivalent oxygen lone pairs (λ_5), two on each oxygen. The calculations were carried out such that the positive z axis is along the C_1C_2 internuclear axis and the enol ring is in the xz plane with the positive x axis pointing into the ring.

λ_1 is a typical CC σ bond, clearly localized on C_1 and C_2 and slightly bent out of the ring in the negative x direction. This contributes 4.00 eV to the CC bond energy which may be compared with a value of 3.81

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(24) K. Ruedenberg, *Rev. Mod. Phys.*, **34**, 326 (1962).

(25) The standard reference molecules and corresponding bond energies are those listed in Table 2.8 of W. J. Moore, "Physical Chemistry," Prentice-Hall, Englewood Cliffs, N. J., 1972.

(26) P. A. Kollman and L. C. Allen, *Chem. Rev.*, 72, 283 (1972), and references cited therein.

(27) M. S. Gordon and W. England, *J. Amer. Chem. Soc.*, **94**, 5168 (1972).

Table II. Localized Orbitals in Acetylacetone

	λ_1	λ_2	λ_3	λ_4	λ_5
C_1 2s	0.4507	0.3631	−0.0126	0.0	−0.0059
$2p_x$	−0.0005	0.4878	+0.0486	0.0	−0.0109
$2p_y$	0.0	0.0	0.0	0.4284	0.2603
$2p_z$	0.5490	−0.2682	+0.0518	0.0	−0.0356
C_2 2s	0.4183	−0.0153	−0.0196	0.0	0.0207
$2p_x$	−0.0399	0.0358	+0.0071	0.0	−0.0102
$2p_y$	0.0	0.0	0.0	0.7864	−0.0583
$2p_z$	−0.5563	−0.0067	+0.0194	0.0	−0.0155
C_3 2s	−0.0025	−0.0172	+0.0107	0.0	−0.0005
$2p_x$	0.0178	0.0131	+0.0190	0.0	−0.0023
$2p_y$	0.0	0.0	0.0	0.4284	−0.0766
$2p_z$	−0.0508	0.0021	−0.0042	0.0	0.0004
O_4 2s	−0.0027	0.3300	0.4647	0.0	0.5221
$2p_x$	0.0068	−0.5771	0.5651	0.0	0.0326
$2p_y$	0.0	0.0	0.0	−0.0505	0.6477
$2p_z$	−0.0113	0.3279	0.5264	0.0	−0.4729
O_5 2s	−0.0095	−0.0008	−0.0479	0.0	0.0020
$2p_x$	0.0179	0.0013	0.0378	0.0	−0.0022
$2p_y$	0.0	0.0	0.0	−0.0505	0.0296
$2p_z$	−0.0096	0.0001	0.0721	0.0	−0.0015
H_6 1s	−0.0020	−0.0102	0.4115	0.0	−0.0192

eV for ethane.[28] The ring CC bonds are further stabilized by λ_4, the three-center π bond, by 0.88 eV. This accounts for most of the calculated bond energy. Such three-center bonds are typical of monosubstituted and some disubstituted benzenes;[29] however, localization of the MO's of unsubstituted benzene yields alternating σ and banana bonds.[20]

As expected from the relatively large internuclear separation and electronegativity difference, the OH bonds are rather highly polarized toward the oxygens. The net charges in these bonds are 1.6248 and 0.3387 on O and H, respectively. In contrast, the corresponding point charges in the OH bond in a typical alcohol, *i.e.*, methanol, are 1.1854 and 0.8134, while the O lone pairs in the same molecule concentrate 1.9707 of the electron density on oxygen. Thus, λ_3 may be viewed as about halfway between a typical lone pair and a typical OH bond. This is rather different from the O-H—O hydrogen bond in the water dimer,[18] which is much more like a perturbed lone pair. That λ_3 and its equivalent counterpart must be considered rather as bonds is emphasized by the concurrent appearance of two lone pairs on each oxygen, as well as by the COH angle of 106° which is typical of COH angles in alcohols.

The CO σ bonds (λ_2) contribute 4.21 eV to the energy of these bonds as compared with 3.95 eV for the similar bond in methanol. While there are no other CO bonds as such, the oxygen lone pairs (λ_5) are rather delocalized onto the adjacent carbon (the charge density on O_4 in λ_5 is 1.8336). As a result, there is significant constructive interference between CO within each lone pair, giving a total contribution of 0.93 eV or 18% of the bond energy.

IV. Conclusions

The most important conclusion to be drawn from this work is that INDO predicts a stable, symmetric planar ring for the enol form of acetylacetone with CC and CO bonds having energies slightly less than averages of isolated single and double bonds. Trifluoro substitution results in a small distortion of the symmetry of the ring with the internally bound hydrogen shifted slightly toward the CF_3 group in such a way that the sum of the two OH bond energies is virtually unchanged. The CC bond on the methyl side of the molecule is weakened by substitution, while the adjacent CO bond and CC bond on the CF_3 side are strengthened.

The OH-localized orbitals behave more like typical OH bonds (albeit more highly polarized) than perturbed lone pairs as is characteristic of weak hydrogen bonds. The hydrogen bonds in ACAC and TFA are also much stronger than most *inter*molecular hydrogen bonds. While the existence of a more flexible geometry (as compared with, for example, the five-membered ring in pyruvic acid[18]) *allows* the type of interaction observed in these molecules, a crucial point here must be that the proton "donor" and "acceptor" are part of the same molecule. This, coupled with ring delocalization (as evidenced by the localized orbitals), facilitates an efficient rearrangement of electron density on hydrogen bond formation.

This hypothesis can be investigated further by carrying out similar calculations on the intermolecular hydrogen bonds between acetone and ethanol, methyl vinyl ketone and ethanol, and vinyl alcohol and acetone. The effect of removing ring delocalization (by partially hydrogenating acetylacetone) on the intramolecular hydrogen bond should also shed some light on this question. This is particularly important since similar considerations should also have an influence on the ability of these molecules to behave as bidentate ligands in transition metal complexes. Finally, in view of the results presented here, it is of interest to reinvestigate the structure of malondialdehyde to determine why Schuster's calculations predict an asymmetric hydrogen bond in this molecule.

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(28) The value 4.00 eV for the contribution to the ACAC CC bond energy from λ_1 is obtained by dividing the negative of the corresponding interference enerby by the average normalization factor as discussed in section II, while 3.81 eV is the experimental bond energy in ethane (ref 25). It might be argued that the latter value should be compared with the ACAC CC interference in λ_1 divided by the appropriate CC single bond normalization factor obtained from the ethane reference molecule. This would give a value of 4.05 eV rather than 4.00 eV, a rather small difference; however, the disadvantage of proceeding in this way is that one would then need a normalization factor specifically for the three-center π bond plus specific factors for each of the tails contributing to the total CC interference energy. These are not available and would in any case give rise to a rather involved procedure. We view the agreement between the two possibilities as justification for the present approach. Similar comments obtain for the ACAC CO bonds.

(29) The localized orbitals of substituted benzenes will be the subject of a later paper.