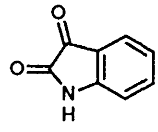
The Influence of Lone-pair Repulsions on C–C Bond Lengths: A Critical Evaluation of the Experimental and Theoretical Evidence

Ananthaiah Rathna and Jayaraman Chandrasekhar *
Department of Organic Chemistry, Indian Institute of Science, Bangalore 560012, India

X-Ray structural data, as well as semiempirical and *ab initio* molecular orbital calculations, reveal no systematic and substantial difference between the C–C bond lengths of *cis* and *trans* 1,2-diketones. Additional results on various conformations of 1,2-diimines and 1,2-dithiones follow the same pattern. Therefore, lone-pair repulsions cannot be implicated in the observed lengthening of C–C bonds in isatin and several related molecules. Conjugation in these systems occurs peripherally avoiding the participation of the central C–C bond. Negative hyperconjugative interaction between the oxygen lone pairs and the adjacent C–C σ^* orbital is suggested to be the principal reason for the relatively long C–C bond in diketones. This effect is found in both the *cis* and *trans* conformations.

In general, C–C single bond lengths are assumed to be constant and quite insensitive to electronic effects. However, in recent years, the possibility of effecting significant changes has attracted considerable attention.[1–5] The relatively long C–C bonds in strained molecules, such as the propellanes, and in sterically crowded molecules are easy to rationalise.[1] Lengthened C–C bonds are also found in molecules with captodative substituents,[2,3] although this electronic effect has not always been recognised as the source of bond stretching. The possibility of bond contraction has also been considered. Several organic systems with exceptionally short C–C bonds due to rehybridisation effects have been studied, both experimentally and theoretically.[4]

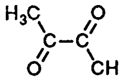
Recently, Palenik *et al.* have postulated another intriguing mode of lengthening C–C bonds,[5] after re-determining the structure of isatin (**1**). The C–C bond length involving the dicarbonyl unit, constrained to be cisoid by the ring geometry, was strikingly large, 1.555 Å (1 Å = 100 pm), compared to the value expected for a single bond between two sp^2 carbon atoms (1.48 Å).[6] A further analysis of structures of *cis*-diketones found in the Cambridge Crystallographic Structural Database (CCSD) indicated this to be a common feature. The bond length varied from 1.506–1.582 Å for 43 molecules, with the average being 1.542 Å. In contrast, C–C bond lengths were shorter in *trans*-diketones (only four were found in the CCSD), ranging from 1.418–1.504 Å, with an average of 1.476 Å. These results were interpreted in terms of lone-pair repulsions involving the carbonyl oxygen atoms, leading to longer C–C bond lengths in *cis*-diketones.

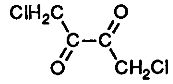

1

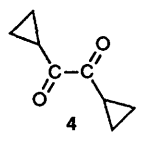
While the presence of lone-pair repulsions in *cis*-diketones cannot be disputed, it is surprising that large changes in bond lengths can result. Bond angles rather than bond lengths are expected to be affected to a significant extent. We have therefore critically examined the proposal of Palenik *et al.* from different angles. The available crystal structures were first analysed. Instead of a statistical analysis of the crystallographic data base, we have chosen to examine the structures of several specific systems, and systematically evaluate the role of heteroatoms, π delocalisation, and repulsions due to bulky substituents on the observed geometries. Further, extensive computational data are also available on diketones at various levels of theory. These results provide useful information concerning the dependence of C–C bond lengths on the relative orientation of the carbonyl units. We have also considered additional systems in which the effect of lone-pair repulsions on bond lengths can be directly examined, *viz.*, 1,2-diimines and 1,2-dithiones. In order to provide a consistent rationale for the experimental and computed variation in bond lengths, additional calculations on model systems have also been carried out.

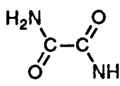
Discussion

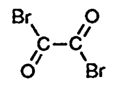
Crystallographic Evidence.—A number of well-defined structures have been published in which *trans*-1,2-diketo units are present. The structure of the simplest molecule of this type, *viz.*, biacetyl **2**, has been thoroughly characterised.[7] The two carbonyl units adopt a perfect *trans* orientation. The central C–C bond length is 1.54 Å. Two related molecules, **3** and **4**, within chloromethyl[8] and cyclopropyl[9] groups instead of the methyl units, also exhibit the same structural features, *viz.* a *trans* alignment of the carbonyl groups and a relatively long central C–C bond (Table 1). These values are well outside the range quoted by Palenik *et al.*[5] (1.418–1.504 Å) for *trans*-diketones. These authors have evidently imposed some constraints in their search of the CCSD which failed to reveal the three structures mentioned here.

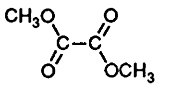

2


3


4


5


6

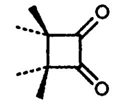

7

The presence of heteroatom substituents at the carbonyl groups does not lead to significant reduction in the C–C bond lengths. Three representative structures (diamide **5**,[10] oxalyl bromide **6**[11] and diester **7**[12]) have unambiguous *trans* arrangement of the dicarbonyl units with relatively long C–C bonds (Table 1). These results clearly demonstrate that neither the inductive effect of the electronegative substituents nor conjugation with the carbonyl units leads to any reduction in

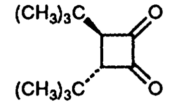
Table 1 X-Ray crystallographic C–C bond lengths/Å connecting two carbonyl groups and the corresponding O=C–C=O torsion angle/°

Molecule		C–C Distance		Torsion angle	Reference
1		1.555		0.0	5
2		1.540		180.0	7
3		1.527		180.0	8
4		1.535		180.0	9
5		1.542		180.0	10
6		1.560		180.0	11
7		1.530		180.0	12
8		1.516		0.0	13
9		1.560		7.6	14
10		1.542		108.4	15
11		1.540		87.3	16
12		1.535		111.5	17
13		1.585		125.8	15
14	r_1	1.531	α_1	109.5	18
	r_2	1.526	α_2	−111.7	
15	r_1	1.524	α_1	158.4	19
	r_2	1.533	α_2	−52.1	
	r_3	1.533	α_3	−11.4	
	r_4	1.545	α_4	172.9	
16	r_1	1.529	α_1	155.8	19
	r_2	1.522	α_2	−55.4	
	r_3	1.530	α_3	−30.0	
	r_4	1.533	α_4	−151.0	

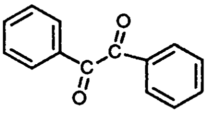
the central C–C separation. In particular, a length of 1.54 Å between two carbonyl groups is not surprising even in sterically unhindered *trans*-diketones. A similar value in isatin or other *cis*-diketones cannot therefore be attributed to 1,4-lone pair repulsions.



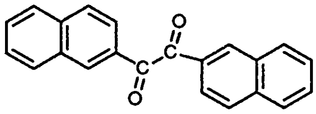
8



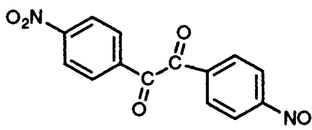
9



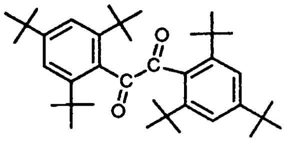
10



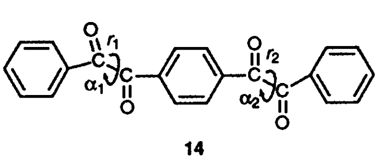
11



12



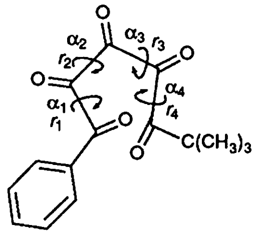
13



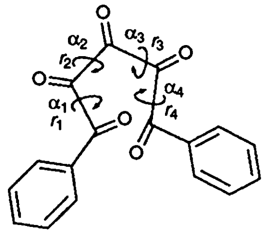
14

It is interesting to consider the C–C bond lengths in diketones which do not adopt the *trans* conformation. Two *cis*-diketones, **8** and **9**, as well as a number of sterically hindered diketones, **10**–**14** with nearly orthogonal arrangement of the dicarbonyl unit are also included in Table 1. While the value in **8** is shorter[13] than that observed in isatin, the related derivative **9** with *tert*-butyl substituents exhibits a longer C–C bond.[14] The perpendicular diketones also have a central C–C bond length around 1.54 Å.[15–18] The severely encumbered derivative **13** has a particularly long C–C bond (1.585 Å).[15] These results again confirm that lone-pair repulsions cannot be the key factor determining the separation between the carbonyl groups.

A dramatic example of the effect of lone-pair (dipole) repulsions on molecular geometry is provided by the structures of two vicinal pentaketones, **15** and **16**, determined recently by Gleiter *et al.*[19] In both compounds, the three central carbonyl groups adopt a cisoid conformation, while the outer units are oriented in a transoid geometry. The C–C bond lengths separating the carbonyl groups do not exhibit the wide variation suggested by the analysis of Palenik *et al.*[5] In **16**, the corresponding bond lengths are remarkably constant, ranging from 1.522–1.533 Å (Table 1). A slightly greater variation is found in the derivative **15**. However, there is no direct relation between the bond length and the torsional angle. While one of the longer bonds with a length of 1.533 Å corresponds to a cisoid diketone, another C–C bond length of 1.545 Å is that of a transoid unit. As discussed in detail by Gleiter *et al.*,[19] the strong dipole interactions present in vicinal polyketones lead to interesting conformational effects with well-defined torsional minima. On the other hand, the effect on C–C bond lengths clearly appears less important.

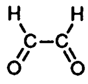


15

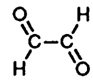


16

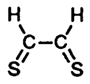
Computational Evidence.—The best procedure with which to evaluate the effect of 1,4-lone-pair interactions on C–C bond lengths would be to directly consider the dependence of the bond length on the torsional angle for a particular model system, keeping all other factors constant. With the possible exception of the results on vicinal polyketones, such internal comparisons are not available experimentally, although a wide variety of structures have been determined. Computational methods are ideally suited for carrying out an analysis of this kind.



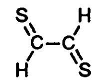
17a



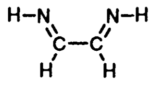
17b



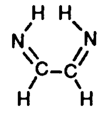
18a



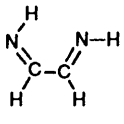
18b



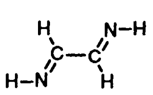
19a



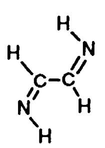
19b



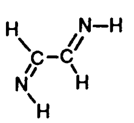
19c



19d



19e



19f

The simplest model system to be considered is glyoxal, **17**, for which optimised geometries have been reported for both the *cis* and *trans* conformations at various levels of theory[20–23] (Table 2). While there is some variation in the geometrical parameters

Table 2 Computered C–C bond lengths/Å in diketones

Molecule	C–C Distance MNDO[a]	DZ or 3–21G	6–31G*
17a	1.524	1.509[b]	1.529[c]
17b	1.529	1.504[b]	1.517[d]
18a	1.472	1.452[e]	1.484[f]
18b	1.475	1.445[e]	1.472[f]
19a	1.485	1.494[g]	1.495[h]
19b	1.490	1.507[g]	1.504[h]
19c	1.488	1.494[g]	1.498[h]
19d	1.490	1.474[g]	1.482[h]
19e	1.492	1.493[g]	1.490[h]
19f	1.492	1.490[g]	1.486[h]
19g	1.513	1.525[a]	—
19h	1.517	1.516[a]	—

[a] This work. [b] Ref. 20. [c] Ref. 22. [d] Ref. 21. [e] Ref. 26. [f] Ref. 27. [g] Ref. 28. [h] Ref. 29.

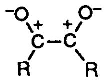
obtained with different methods, all procedures uniformly indicate that the C–C bond length does not significantly depend on the relative orientation of the carbonyl units. At the highest theoretical levels considered, employing the 6–31G* or equivalent basis sets with double zeta plus polarisation functions,[23] the C–C bond length increases by a little over 0.01 Å on going to the *cis* form of glyoxal. Other theoretical procedures predict an even smaller change. Interestingly, the reported electron diffraction structure[24] of *trans*-glyoxal has a slightly longer C–C bond length than in the *cis* form determined by rotational spectroscopy,[25] although this finding has been questioned on the basis of high level calculations.[23] The computed bond length in the C_2 transition state for the internal rotation process is also found to be virtually identical to that in the *cis* conformer. Thus, the C–C bond length variation of the order of 0.06 Å suggested by Palenik *et al.*[5] is not found in glyoxal in any of the conformations considered.

Computed geometries of additional model systems can also be analysed to probe the effect of dipole interactions on C–C bond lengths. The structural parameters of the *cis* and *trans* conformers of dithioglyoxal, **18**, have been obtained at various levels of theory[26,27] (Table 2). The differences in C–C bond lengths parallel the data obtained for glyoxal. Only a marginal lengthening of the C–C bond in the *cis* form is noted.

The various conformers of the 1,2-diimines **19a–f** provide an ideal means of evaluating lone-pair interactions. Of particular interest are the three *cis* conformers. In **19a**, the nitrogen lone-pairs are aligned for maximum repulsion. In **19b**, non-bonded hydrogen interactions should contribute significantly. In the third form, **19c**, an attractive intramolecular interaction involving a nitrogen lone-pair and an adjacent N–H bond is expected. In spite of these widely differing factors, the computed C–C bond lengths are virtually unchanged for the three conformers at the MNDO as well as *ab initio* levels.[28,29] The magnitude of the variation in the C–C distance is nearly the same for the three equivalent *trans* conformers (Table 2). The maximum difference in the C–C bond lengths in the six conformers is only about 0.02 Å, and even this change cannot entirely be attributed to lone-pair repulsions (*vide infra*).

Factors Determining the Central C–C *Bond Length in* 1,2-*Diketones*.—The long C–C bond (1.555 Å) involving two sp^2 carbon atoms in isatin is certainly remarkable, as noted by Palenik *et al.*[5] However, the analyses presented above show that the geometric feature is not primarily due to the lone-pair repulsions in the cisoid diketone. Several *trans* diketones also have a relatively long C–C bond. In the following discussion, we consider various factors which can contribute to this unusual geometric effect.

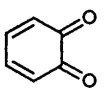
The nature of π interactions in diketones is obviously an important factor to consider. Palenik *et al.* have argued that any reasonable resonance structure would contribute double bond character to the central C–C bond. On the other hand, Eriks *et al.*[7] have postulated that the highly electronegative nature of oxygen would make the highly ionic form, **20**, contribute significantly in these molecules. The central carbon



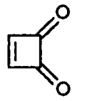
20

atoms would thus retain a single bond. Electrostatic interactions between the formal positive charges on the carbon atoms would lead to a lengthening of the C–C bond. This explanation would account for the relatively long bond in *trans*-diketones as well.

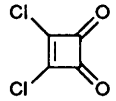
The nature of π polarisation in diketones can be ascertained by comparing the geometries of **21** and **22** in which the carbonyl units are fused to conjugated rings. While enhanced double-bond character between the carbonyl units would contribute to benzenoid stability of *o*-quinone, the di-ionic resonance structure should be favoured in **22**. The C–C separation between the carbonyl units is 1.545 and 1.554 Å, respectively, at the MNDO level. The experimental geometries of **21** and the dichloro derivative **23** reveal the same pattern (1.552 and 1.560 Å).[30,31] These results suggest that resonance structure **20** is more important than any alternative with double-bond character between the carbon atoms, even in the most favourable situation such as **21**.



21



22

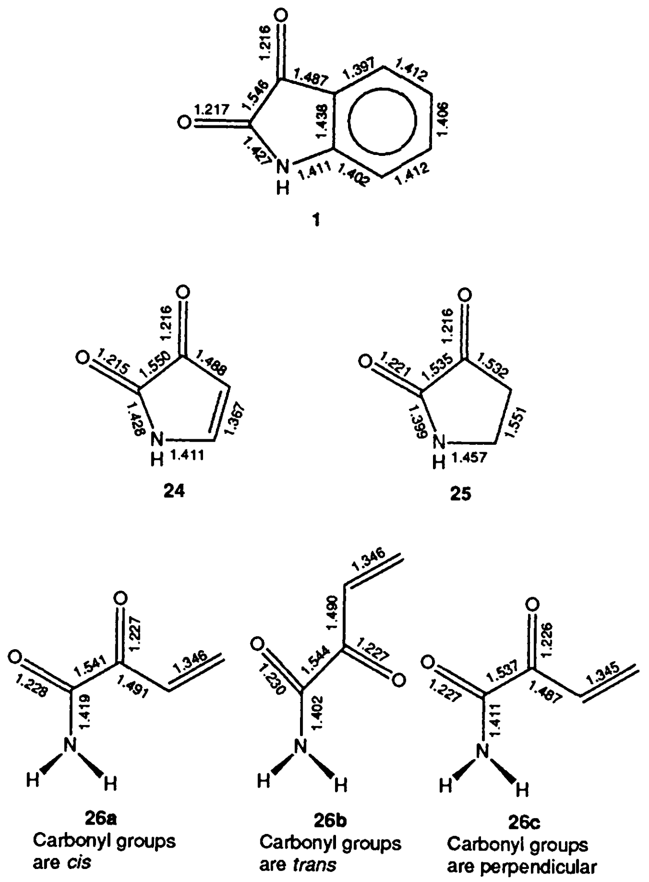


23

The above description is valid when additional π donor groups are placed on the carbonyl fragments. The ionic form of the carbonyl bond is stabilized by the substituent. Thus, conjugation does not enhance the double-bond character of the C–C bond. Rather, delocalisation is effective peripherally, avoiding the central bond. Consistent with this analysis, the central C–C bond is quite long in oxamide and oxalyl bromide (Table 1). The unimportance of conjugation across the C–C bond is dramatically reflected in the nearly orthogonal orientation of the carbonyl groups in several oxamides and α-ketoamides, including the immunosuppressant agents FK506 and rapamycin.[32] Recently, even the oxalate dianion has been suggested to prefer the perpendicular D_{2d} geometry in the free state.[33]

The same bonding effects are also operative in isatin, as revealed by MNDO results on **1** and the related model systems **24–26** (Fig. 1). The long C–C bond between the carbonyl groups of isatin is correctly reproduced by the theoretical method. The smaller five-membered ring model compound **24** is computed to have a similar C–C bond length. In order to probe whether the ring structure has any effect on the magnitude of conjugation, the acyclic analogue, **26**, was examined. This molecule was also computed to have a relatively long C–C bond, in the *cis*, *trans*, and the most stable orthogonal conformations of the carbonyl units. Conjugation is seen to avoid the central C–C bond in all these systems.

While the di-ionic resonance structure for 1,2-diketones would account for the relative lengthening of the C–C bond, another factor may also contribute. The HOMO of the carbonyl



1

24

25

26a
Carbonyl groups
are *cis*

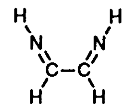
26b
Carbonyl groups
are *trans*

26c
Carbonyl groups
are perpendicular

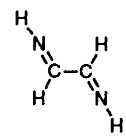
Fig. 1 MNDO optimized bond lengths/Å in isatin and related model compounds

group is a relatively high energy p-type lone-pair orbital.[34] This orbital can have a stabilising two-electron interaction with adjacent σ^*_{CC} orbitals. This would lead to a reduction in the C=O bond and a lengthening of the C–C bond. However, the smaller force constant associated with the C–C bond and the combined effect of two carbonyl units on either side of the C–C bond would make the latter geometric distortion more pronounced. Interestingly, this negative hyperconjugative effect[35] would operate irrespective of the conformation of the diketone, in agreement with the experimental and theoretical evidence. Much larger geometric distortions due to negative hyperconjugation involving carbonyl lone-pairs have been computed in other more favourable systems.[36]

A convenient system in which the relative importance of negative hyperconjugative interactions can be gauged is the diimine molecule mentioned earlier. The C–C bond length in the various conformations involving the N–H bonds is on average slightly higher than the standard value of 1.48 Å expected for two sp^2 carbon atoms. The di-ionic resonance form seems to be quite insignificant, in spite of the electronegative nature of nitrogen. The variation in the C–C bond lengths is also modest, in spite of the changes in potential (hydrogen–hydrogen and lone pair–lone pair) repulsive and (hydrogen bonded) attractive interactions in the different conformers. Interestingly, when the imine nitrogen atoms are forced to have linear coordination, the most lengthened C–C bond is obtained. Geometry optimisation at the 3-21G level on this model system with *cis* and *trans* imine units (**19g** and **19h**) yield a central bond length of *ca.* 1.52 Å (Table 2). In the linearised form of the imines, the nitrogen lone-pairs lose their 's' character and hence are higher in energy. The in-plane p-type lone-pair orbitals can take part in negative hyperconjugation with the C–C σ* orbital more effectively, leading to a longer C–C bond. The stretching produced by this effect is greater than the changes produced by the ionic character of the C=N bonds as well as by other intramolecular attractive and repulsive interactions.



19g



19h

The calculated (MNDO) charges, bond orders and two-centre electronic energies of α-diketones (Table 3) provide support for the above analysis of the factors determining C–C bond lengths. The highly polarised nature of the carbonyl bonds is confirmed by the relatively large π-charges. The oxygen atoms bear a charge of nearly −0.25 in glyoxal (**17**) and biacetyl (**2**). The C–C π bond order (0.14) is small in both molecules, but not entirely negligible. Therefore, the nature of the atomic charges in diketones is only partly responsible for the lengthening of the central C–C bond.

The effect of additional conjugating groups on the computed charges and bond orders is in line with the earlier analysis. Thus, constraining the dicarbonyl fragment in potentially anti-aromatic and aromatic rings (**21** and **22**) does not significantly alter the π polarisation as well as the C–C π bond order. Further, the peripheral nature of π delocalisation in oxamide is reflected in the increased carbonyl polarisation, while leaving the C–C π bond order unaffected. Similar data are obtained for isatin **1** and its acyclic models, *e.g.*, **26b** (Table 3). Clearly, the nature of orbital interactions in diketones are similar in *cis* and *trans* conformations.

In contrast to diketones, the di-ionic structure is less important for dithioglyoxal (**18**) and the diimine **19**. The C–C π bond order is also higher, consistent with the reduced C–C bond lengths in these systems.

The calculated data in Table 3 also substantiate the role of negative hyperconjugation in increasing C–C bond lengths. The C–C σ bond orders in various diketones are much less than 1 (*ca.* 0.7). Correspondingly, C–O σ bond orders are quite high. The interaction between the oxygen in-plane lone-pair orbital with the C–C σ* orbital would account for these computed bond orders. Energy partitioning data provide additional support. The effect is especially evident in the various conformers of diimine, **19**. Interactions involving the lone pairs and the hydrogen atoms produce no significant variation in the C–C two-centre energy contributions. However, when the N–H bonds are linearised (**19g** and **19h**), the C–C energy term is reduced by *ca.* 1.5 eV. The change is clearly indicative of enhanced negative hyperconjugation in these conformers due to the higher energy nitrogen lone-pairs, as discussed above.

Conclusions

The unusually long C–C bond separating the carbonyl units of isatin is not entirely due to the forced *cis* conformation of the diketone. Several *trans* diketones have been experimentally shown to have relatively long bonds. Theoretical calculations also confirm that the C–C bond lengths in 1,2-diketones are relatively insensitive to the conformation of the carbonyl units. Repulsive lone-pair interactions cannot be held responsible for the C–C bond lengths in these molecules.

The long C–C bond in 1,2-diketones may be explained on the basis of significant contribution from the di-ionic resonance form. Conjugation effects due to π donor substituents occur without involving the central C–C bond, leaving its length unaffected. An additional electronic effect, *viz.*, negative hyperconjugative interaction between the carbonyl n(p) lone-

Table 3 MNDO charges and bond orders in α-diketones and related model systems

Molecule	Atom	π-Charge	Bond	Bond order π	Bond order σ	Two-centre energy (eV)
17a	C	0.25	C–C	0.15	0.70	−14.00
	O	−0.25	C–O	0.96	1.04	−27.36
17b	C	0.26	C–C	0.14	0.70	−13.91
	O	−0.26	C–O	0.95	1.04	−27.30
2	C	0.25	C–C	0.13	0.71	−13.83
	O	−0.27	C–O	0.95	1.01	−26.93
21	C	0.23	C–C	0.14	0.66	−13.90
	O	−0.25	C–O	0.93	1.05	−26.95
22	C	0.25	C–C	0.12	0.72	−12.56
	O	−0.29	C–O	0.93	1.02	−27.70
5	C	0.23	C–C	0.13	0.71	−13.92
	O	−0.40	C–O	0.85	0.97	−26.53
1	C	0.24	C–C	0.12	0.70	−13.49
		0.24				
	O	−0.35	C–O	0.87	1.03	−27.21
		−0.28		0.92	1.04	−27.44
26b	C	0.23	C–C	0.13	0.71	−13.84
		0.25				
	O	−0.39	C–O	0.86	0.97	−26.50
		−0.30		0.92	1.00	−26.88
18a	C	0.20	C–C	0.27	0.73	−16.17
	S	−0.20	C–S	0.94	0.93	−19.49
18b	C	0.21	C–C	0.26	0.74	−16.07
	S	−0.21	C–S	0.94	0.94	−19.39
19a	C	0.09	C–C	0.20	0.76	−15.86
	N	−0.09	C–N	0.98	0.99	−24.86
19b	C	0.11	C–C	0.19	0.75	−15.55
	N	−0.11	C–N	0.98	0.99	−24.88
19c	C	0.09	C–C	0.20	0.77	−15.67
		0.11				
	N	−0.09	C–N	0.98	0.99	−24.99
		−0.11		0.97	0.99	−24.79
19d	C	0.12	C–C	0.19	0.76	−15.75
	N	−0.12	C–N	0.97	0.99	−24.82
19g	C	0.15	C–C	0.17	0.68	−14.16
	N	−0.15	C–N	0.97	1.00	−28.35
19h	C	0.16	C–C	0.16	0.69	−14.11
	N	−0.16	C–N	0.97	0.99	−28.31

pairs and the C–C σ* orbital, is also suggested to play an important role in the lengthening of the central C–C bond in 1,2-diketones.

Acknowledgements

We thank P. v. R. Schleyer for discussions and M. Yanez for the detailed 6-31G* geometries of **19a–f** from ref. 29.

References

1 E. Osawa and K. Kanematsu, in *Molecular Structure and Energetics*, eds. J. E. Liebman and A. Greenberg, VCH Publishers, Weinheim, Federal Republic of Germany, 1986, vol. 3; E. Osawa, Y. Onuki and K. Mislow, *J. Am. Chem. Soc.*, 1981, **103**, 7475.

2 B. Tinant, S. Wu, J.-P. Declercq, M. van Meersche, W. Masamba, A. de Mesmaeker and H. G. Viehe, *J. Chem. Soc., Perkin Trans. 2*, 1988, 1045.

3 G. M. Anstead, R. Srinivasan, C. S. Peterson, S. R. Wilson and J. A. Katzenellenbogen, *J. Am. Chem. Soc.*, 1991, **113**, 1378; K. Venkatesan, T. R. Kasturi, B. Rajashekar, G. J. Raju, G. M. Reddy, R. Sivaramamakrishnan and N. Ramasubbu, *J. Chem. Soc., Perkin Trans. 1*, 1984, 2375.

4 A. Rathna and J. Chandrasekhar, *J. Mol. Struct.*, (*THEOCHEM*), 1991, **228**, 249; P. v. R. Schleyer and M. Bremer, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1226; O. Ermer, P. Bell, J. Schafer and G. Szeimies, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 473; A. C. Friedli, P. Kaszynski and J. Michl, *Tetrahedron Lett.*, 1989, **34**, 455; G. S. Murthy, K. Hsssenruck, V. M. Lynch and J. Michl, *J. Am. Chem. Soc.*, 1989, **111**, 7262; F. H. Allen, *J. Org. Chem.*, 1989, **54**, 6096; R. Gilardi, M. Maggini and P. E. Eaton, *J. Am. Chem. Soc.*, 1988, **110**, 7232; U. Bunz, K. Polborn, H.-U. Wagner and G. Szeimies, *Chem. Ber.*, 1988, **121**, 1785; O. Kaszynski and J. Michl, *J. Am. Chem. Soc.*, 1988, **110**, 5225; H. Irngartinger, R. Jahn and H. Rodewald, *J. Am. Chem. Soc.*, 1987, **109**, 6547; F. H. Allen, *Acta Crystallogr., Sect. B*, 1984, **40**, 64; M. N. Paddon-Row, K. N. Houk, P. Dowd, P. Garner and R. Schappert, *Tetrahedron Lett.*, 1981, **22**, 4799; H. Irngartinger, A. Goldmann, R. Schappert, P. Garner and P. Dowd, *J. Chem. Soc., Chem. Commun.*, 1981, 455; H. Irngartinger and K. L. Lukas, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 694.

5 G. S. Palenik, A. E. Koziol, A. R. Katritzky and W.-Q. Fan, *J. Chem. Soc., Chem. Commun.*, 1990, 715.

6 F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1987, S1.

7 K. Eriks, T. D. Hayden and I. Y. Chan, *J. Am. Chem. Soc.*, 1983, **105**, 3940.

8 P. B. Ducourant, C. Maury, J.-P. Lere-porte, J. Petrissans and J. L. Ribet, *Acta Crystallogr., Sect. B*, 1986, **42**, 341.

9 C. N. A. Lute and C. H. Stam, *Recl. Trav. Chim. Pays-Bas*, 1976, **95**, 130.

10 E. M. Ayerst and J. R. C. Duke, *Acta Crystallogr.*, 1954, **7**, 588.

11 P. Groth and O. Hassel, *Acta Chem. Scand.*, 1962, **6**, 2311.

12 M. W. Dougill and G. A. Jeffrey, *Acta Crystallogr.*, 1953, **6**, 831.

13 C. D. Shirrel and D. E. Williams, *Acta Crystallogr., Sect. B*, 1974, **30**, 245.

14 J. K. Coleman, S. C. Neely and D. V. D. Helm, *Acta Crystallogr., Sect. B*, 1976, **32**, 115.

15 E. J. Gabe, Y. L. Pace, F. L. Lee and L. R. C. Barclay, *Acta Crystallogr., Sect. B*, 1981, **37**, 197.

16 S. C. Biswas, M. Mukherjee, S. Ray and R. K. Sen, *Chem. Phys. Lett.*, 1985, **113**, 498.

17 R. E. McClauney and W. H. Watson, *Acta Crystallogr., Sect. B*, 1979, **35**, 4831.

18 A. Syed and E. D. Stevens, *Acta Crystallogr., Sect. C*, 1984, **40**, 1273.

19 R. Gleiter, E. Litterest, T. Oeser and H. Irngartinger, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 1048.

20 R. A. Whiteside, M. J. Frisch, J. S. Binkley, D. J. DeFrees, H. B. Schlegel, K. Raghavachari and J. A. Pople, *Carnegie-Mellon Quantum Chemistry Archive*, Pittsburgh, 1981.

21 H. D. Goddard, H. Yu and W. Chan, *J. Am. Chem. Soc.*, 1990, **112**, 7529.

22 P. v. R. Schleyer, P. H. M. Buzelaar, D. Cremer, M. Wallasch and E.-U. Würthwein, *J. Am. Chem. Soc.*, 1987, **109**, 6290.

23 Y. Osamura and H. F. Schafer III, *J. Chem. Phys.*, 1981, **74**, 4576.

24 K. Kuchitsu, T. Fukuyama and Y. Morino, *J. Mol. Struct.*, 1969, **4**, 41.

25 D. A. Ramsay and C. Zauli, *Acta Phys. Acad. Sci. Hung.*, 1974, **35**, 79; A. R. H. Cole, Y. S. Li and J. R. Durig, *J. Mol. Spectrosc.*, 1976, **61**, 346.

26 R. C. Haddon, S. R. Wasserman, F. Wudl and J. R. J. Williams, *J. Am. Chem. Soc.*, 1980, **102**, 6687.

27 J. D. Goddard, *J. Comput. Chem.*, 1987, **8**, 389.

28 D. E. Bernholdt, J. D. Irwin, J. P. Lacosse, K. J. Mattason and J. B. Miers, *J. Mol. Struct. (THEOCHEM)*, 1987, **153**, 175.

29 O. Mo and M. Yanez, *J. Mol. Struct. (THEOCHEM)*, 1989, **201**, 17.

30 A. L. Macdonald and J. Trotter, *J. Chem. Soc., Perkin Trans. 2*, 1973, 476.

31 R. Mattes and S. Schroebler, *Chem. Ber.*, 1972, **105**, 3761.

32 G. Adiwidjaja and J. Voss, *Chem. Ber.*, 1977, **110**, 1159; H. Tanaka, A. Kuroda, H. H. Marusawa, H. Hatanaka, T. Kino, T. Goto, M. Hashimoto and T. Taga, *J. Am. Chem. Soc.*, 1987, **109**, 5031; D. C. N. Swindells, P. S. White and J. A. Findlay, *Can. J. Chem.*, 1978, **56**, 2491; M. W. Albers, C. T. Walsh and S. L. Schreiber, *J. Org. Chem.*, 1990, **55**, 4984.

33 M. J. S. Dewar and Y. Zheng, *J. Mol. Struct. (THEOCHEM)*, 1990, **209**, 157.

34 W. L. Jorgensen and L. Salem, *The Organic Chemist's Book of Orbitals*, Academic Press, New York, 1973.

35 P. v. R. Schleyer and A. J. Kos, *Tetrahedron*, 1983, **39**, 1141; A. E. Reed and P. v. R. Schleyer, *J. Am. Chem. Soc.*, 1987, **109**, 7362; 1990, **112**, 1434.

36 P. V. Sudhakar and J. Chandrasekhar, *J. Mol. Struct. (THEOCHEM)*, 1989, **194**, 135.

Paper 1/02279B
Received 15*th May* 1991
Accepted 2*nd July* 1991