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BOND LENGTHENING AND THROUGH-BOND INTERACTIONS IN p,p'-DIBENZENE AND RELATED MOLECULES

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Abstract—The structure of p,p'-dibenzene (PDB) has been investigated by full geometry optimizations using the empirical force field (EFF) and MINDO/3 methods. While other structural parameters are in good agreement, the central bond length calculated by MINDO/3 (1.595 Å), as confirmed by an *ab initio* (STO-3G basis set) optimization (1.596 Å), is in striking contrast to the corresponding length calculated by EFF (1.543 Å). A detailed analysis of the electronic structure of PDB based on a quantitative perturbational molecular orbital treatment reveals that through-bond coupling of the four π systems is responsible for an elongation of the σ bond which mediates this interaction. Further studies using the EFF and MINDO/3 approaches demonstrate that extended C–C single bonds can arise even in structures with fewer than four π systems. The effect of substituents on the central bond length in PDB has been briefly investigated (MINDO/3). A variety of other structures have been identified in which bond lengthening may result from through-bond coupling.

Through-bond interactions of π systems have been the subject of continued interest[1] since Hoffmann and coworkers[2] first developed the concept 10 years ago. Recently, it was suggested[3,4] that through-bond interactions can cause a significant lengthening of the σ bond which mediates the coupling of the π systems. Our preliminary study[4] was based on a comparison of bond lengths calculated by an empirical force field (EFF) method with the experimental values, and calculations of CNDO/2 overlap populations. We now report the results of a more extensive study of this effect, based on an application of several different computational techniques to the molecular and electronic structure of p,p'-dibenzene (PDB) and related molecules. PDB was chosen as a model system since it is the simplest framework which contains the essential feature of interest: a rigid structure with four π systems capable of effective interaction with a σ bond (Fig. 1). At the same time, PDB is a molecule of theoretical interest in its own right, both as a member of the much studied $(CH)_{12}$ family of compounds,[5] and in relation to orbital symmetry rules, since the concerted thermal dissociation of PDB into two benzene molecules is disallowed.[6]

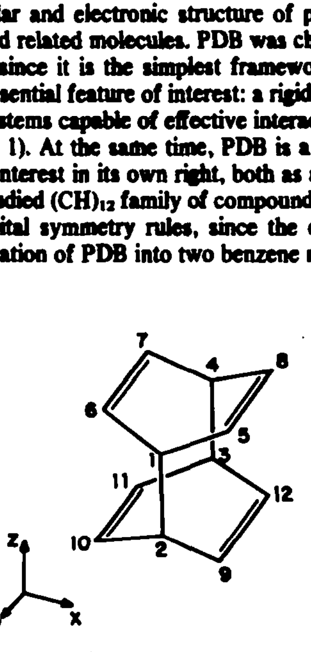


Fig. 1. Structure of p,p'-dibenzene. For the symmetry designations of the molecular orbitals, define three mirror planes, m_x, m_y and m_z, perpendicular to the x, y and z axes, respectively. Relative to a mirror plane m_i, orbitals can be either symmetric, S_i, or antisymmetric, A_i. Subscripts are dropped when all three descriptors are used, e.g. $S_xS_yA_z$ = SSA.

Methods

Several different computational methods were applied to PDB and related structures. The EFF method has been shown to be an effective means of obtaining reliable information on structure and energy for a wide variety of molecules, most successfully for hydrocarbons.[7] The force field used in the present work is one developed by Allinger.[8] Structures were optimized without symmetry constraints using the pattern search minimization technique with an energy criterion for minimization of 0.01 kcal/mol over one iteration.

Semi-empirical MO calculations were carried out primarily using MINDO/3.[9] While this method has been the subject of some recent controversy,[10] the need for complete geometry optimization throughout much of this work, coupled with the efficient geometry optimization scheme included in MINDO/3, make it the method of choice. Errors attributable to the semi-empirical method are mitigated by the fact that our primary concern is with *trends* within a very restricted class of structures.

The neglect of overlap is known to lead to significant differences in the results obtained by NDO methods as compared to *ab initio* or extended Hückel theory (EHT) methods (e.g. ref. 11). Accordingly, *ab initio* calculations were used to test some of the more crucial aspects of the MINDO/3 results. Non-empirical MO calculations were performed with the GAUSSIAN 70 program package using the minimal STO-3G basis set.[12] EHT calculations[13] were also performed on several key structures.

p,p'-*Dibenzene* (*PDB*)

Molecular structure. The results of EFF and MINDO/3 geometry optimizations on PDB are shown in Table 1. The most striking feature of the data is the large difference in C1–C2 bond length calculated by the two methods. The significantly longer bond calculated by MINDO/3 can be taken as direct evidence for a bond lengthening electronic effect which is not included in the EFF.[4] For all other structural parameters there is reasonably good agreement between the two methods, including the molecular symmetry (D_{2h}), and most of the

Table 1. Calculated structural parameters for PDB

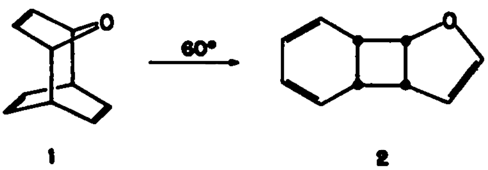
Atomic Parameters	EFF	MINDO/3 [b]
	Bond Lengths (Å)	
C1-C2	1.543	1.595
C1-C5	1.511	1.536
C5-C8	1.336	1.354
C5-C9[a]	2.722	2.821
C1-C4[a]	2.737	2.809
	Bond Angles (deg)	
C2-C1-C5	113.0	113.5
C5-C1-C6	105.4	103.4
C2-C1-H1	113.5	107.0
C5-C1-H1	105.6	109.7
C1-C5-C8	117.6	118.3
C1-C5-H5	117.4	118.2
C8-C5-H5	119.4	123.5

[a] Non-bonded distances. [b] All C-H bond lengths were kept fixed at 1.09 Å. Heat of formation = 135.4 kcal/mol.

major differences are attributable to deformations in the EFF structure caused by close non-bonded contacts which are relieved by the bond lengthening in the MINDO/3 structure.

The C1–C2 bond length in PDB was also optimized using *ab initio* MO calculations. Apart from the central bond length, all structural parameters were fixed at the MINDO/3 optimized values. Structures with bond lengths of 1.545, 1.595 (total energy: −455.73108 au) and 1.645 Å were calculated using the STO-3G basis set, and a parabolic interpolation of total energy vs bond length yielded an optimum value of 1.596 Å, in excellent agreement with the MINDO/3 result. The bond lengths calculated by both MO methods are in good agreement with experimental values for the analogous bond lengths in 9,9′,10,10′-dianthracene[14] (1.61 Å) and related molecules.[4] It thus appears that PDB is a suitable prototype for the study of the bond lengthening effect; furthermore, the excellent agreement between the semi-empirical and the *ab initio* results inspires confidence that the MINDO/3 method will prove adequate for this type of system.

The significant extension of the C1–C2 bond predicted by the MINDO/3 and *ab initio* methods suggests that PDB is likely to be an unstable molecule even though concerted, electrocyclic dissociation of PDB to two molecules of benzene is disallowed.[6] Indeed, a close analog (1) of PDB has been found[15] to be thermally unstable with respect to a Cope rearrangement to 2, which is not expected (see below) to possess bonds as weakened as those in 1.



1 2

Electronic structure. The energies and symmetries (see Fig. 1 for symmetry designations) of the highest lying occupied orbitals as determined by the STO-3G, MINDO/3 and EHT methods for PDB are listed in Table 2. The agreement among the three methods in the relative ordering of orbitals is quite good. The only inconsistency involves the orbital with AAA symmetry, which MINDO/3 places two levels higher than STO-3G, while EHT places it only one level higher. Since this orbital is primarily a framework σ bonding orbital according to all three methods, this discrepancy is an illustration of the well known tendency of semi-empirical methods to yield high lying σ orbitals.[16] However, this discrepancy does not significantly lessen the value of the semi-empirical results, since the symmetry of the AAA orbital disallows interaction with the orbitals responsible for the bond lengthening effect.

The through-bond coupling of the π systems in PDB is evident from the ordering of the four highest lying (STO-3G results) occupied MO's (Table 2), which are primarily the symmetry adapted combinations of the four C–C double bond π systems. Given the D_{2h} symmetry of PDB, only orbitals with S_x symmetry can have a contribution from the p_z orbitals which form the C1–C2 and C3–C4 bonds; it follows that only these orbitals can be involved in through-bond coupling of the π systems. As evidence for the through-bond effect, observe that the SSA orbital lies well below the SSS orbital, i.e. the anti-symmetric combination of the top and bottom π systems is lower in energy than the symmetric combination, contrary to what would be expected in the absence of through-bond interactions. This reversal in orbital sequence is the most characteristic result of through-bond coupling.[1–3] The more conventional ordering (symmetric below antisymmetric) is seen for orbitals of A_x symmetry, for which only through-space interactions can occur.

The orbitals discussed above are all occupied, but the same effects are demonstrated in the unoccupied, π^* orbitals. Again, all three methods lead to the same general conclusion.

The overall orbital mixing picture for PDB which emerges from these calculations is similar in essence to that of a standard example used to illustrate through-bond coupling, 1,4-butanediyl,[3] and to the qualitative interaction diagram used previously to describe the bond

Table 2. Energies and symmetries of highest occupied MO's of PDB[a]

Type	Symmetry[b]	Orbital Energy (ev)		
		STO-3G	MINDO/3	EHT
π	ASA	- 6.484	- 8.814	-11.998
π	SSS	- 7.627	- 8.857	-12.247
π	ASS	- 7.948	- 9.573	-12.610
π	SSA	- 8.508	-10.089	-12.936
σ	AAA	- 9.568	- 9.424	-12.642
σ	SSA	-10.939	-10.336	-13.179

[a] All results are for the MINDO/3 optimized geometry. [b] See Figure 1 for definition of symmetry elements.

lengthening effect.[4] Two separate mixings result, one between orbitals of S_y symmetry (i.e. π bonding orbitals) and one between A_y (π*) orbitals. The effect of the former is to mix σ* character into an occupied orbital (π→σ* donation), resulting in partial occupation of a σ* orbital and in bond lengthening. The other interaction, σ→π* donation, should also lead to a bond lengthening by partial depopulation of a σ bonding orbital.

In the hope of gaining a more quantitative insight into the interplay of π→σ* and σ→π* donations and to guide studies on substituent effects (see below), we performed a quantitative perturbational molecular orbital (PMO) analysis on PDB. The method used[17] involves the dissection of the molecule into fragments and the quantitative calculation of the fragment orbitals and their energies. The fragment orbitals are then allowed to interact to form the full MO's, and an estimate of the relative importance of such interactions in forming the final wave function can be obtained. Since both the PMO analysis and the definition of the fragment orbitals are obtained within the SCF-MO framework, the analysis is as reliable as the SCF calculation itself. It should be emphasized that such a treatment considers all interactions and does not allow for simplification or modification of the PMO analysis by adjustment of parameters. The PMO analyses were based on MINDO/3 calculations.

Our initial fragment analysis defined the C1–C2 and C3–C4 σ bonds along with the associated hydrogens as one fragment and the π system (the remaining atoms) as a second fragment. The mixing of these two fragments to give the MO's of PDB resulted in a complex interaction scheme because of the many σ bonds that were broken. However, it was possible to extract some information about the through-bond coupling from this analysis. A relevant portion of the σ–π interaction diagram is shown in Fig. 2.

The ASA and ASS π orbitals, which are not affected by through-bond coupling, are perturbed when the two fragments are combined to form the molecule. Their energies are raised a small amount by interaction with lower lying doubly occupied orbitals of the appropriate symmetry.

The SSS π orbital interacts strongly with the σ bonding orbital, as required by the through-bond coupling mechanism. The SSA π contributes to a pair of molecular orbitals (this is due to mixing between two nearly degenerate orbitals, one of which is of framework σ type and the other, the π orbital of interest). There is a net lowering in the energies of these, relative to the fragment SSA π orbital, due to an interaction with the SSA σ*. It is this π→σ* interaction that is responsible, in part, for the bond lengthening.

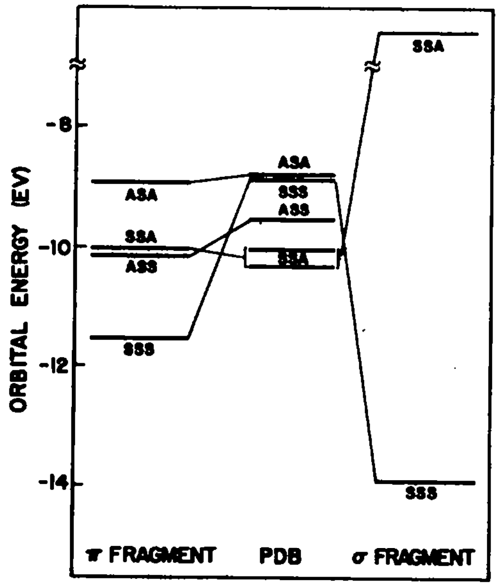


Fig. 2. Diagram of selected orbital interactions resulting from σ–π fragment analysis of PDB. Only interactions leading to S_y orbitals are considered. All PDB orbitals shown are occupied.

The importance of the other possible mechanism, σ→π* donation (orbitals of A_y symmetry), cannot be extracted easily from an analysis based on the above choice of fragments. In addition, the complexity of the remaining interactions that have not been discussed make this approach unsuitable for the analysis of substituent effects. An alternative fragment decomposition was therefore tried in which the two fragments corresponded to the "top" (the atoms above mirror plane m_z) and "bottom" halves of the PDB structure. This decomposition of PDB into two distorted (boat) benzene fragments leads to an overall simpler interaction diagram from which certain important interactions can be clearly discerned. The nature of the interactions considered will necessarily be different than in the σ–π fragment scheme, in contrast to the molecular wave function, which must be the same. A relevant portion of the interaction diagram is given in Fig. 3.

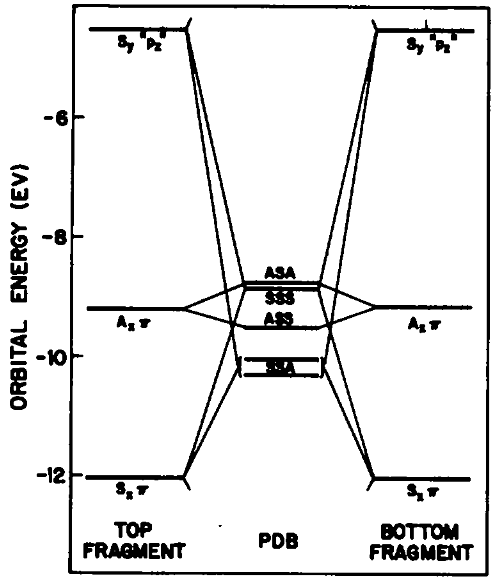


Fig. 3. Diagram of selected orbital interactions resulting from top-bottom fragment analysis of PDB. Only interactions leading to S_y orbitals are considered. All PDB orbitals shown are occupied.

Recombination of benzene fragments into MO's for PDB can be considered in two steps. First, identical orbitals from the top and bottom fragments are combined in pairs, to yield sets of symmetric and antisymmetric orbitals (with respect to mirror plane m_z) and then orbitals of the same symmetry are mixed further. An interaction corresponding to the first step is shown for the two A_x π orbitals that form the ASS and ASA π type MO's. The most prominent interaction of the fragments involves the formation of the S_y σ and σ* orbitals, which can then mix further with the SSS and SSA π orbitals formed from the S_x π fragment orbitals. Comparison of the amount of σ* character in the SSA π orbitals (a measure of the π→σ* donation) with the amount of π* character in an SAS σ bonding orbital (similar analysis, but not shown in Fig. 3) indicates that π→σ* donation is dominant. An analysis based on second order perturbation theory reveals that this dominance results from a larger interaction matrix element, rather than from a smaller energy gap between the interacting orbitals; the larger matrix element for π→σ* interaction parallels the greater overlap expected between π and σ* orbitals as compared to that between σ and π* orbitals.

Since the top-bottom fragmentation scheme also leads to a rationalization of the central bond lengthening, and since the overall interaction diagram is considerably simplified, this method was used to guide the search for substituent effects (see below).

Derivatives of PDB

Hydrogenated derivatives. In all of the compounds studied previously,[4] as well as in PDB, the long bonds are surrounded by four π systems. It was therefore of interest to study systems in which σ bonds are aligned with fewer than four π systems. Our approach hinged on a comparison of structures obtained by EFF and MINDO/3. The results of our calculations on six hydrogenated derivatives of PDB are shown in Table 3. The EFF calculations were performed without symmetry constraints. With the exception of PDB, each molecule relaxed to give a structure with the symmetry of its rotational subgroup. The MINDO/3 structures were optimized with each molecule constrained to its maximum symmetry (Table 3). In the case of the octahydro derivative, when the MINDO/3 final structure was distorted to a D_2 structure and then allowed to relax, the original D_{2h} structure resulted.

According to the MINDO/3 results, successive hydrogenation of PDB leads to a progressive shortening of the long C1–C2 bond, in accord with the diminishing number of potential through-bond interactions. In contrast, EFF results indicate that hydrogenation of PDB causes C1–C2 bond lengthening, in accord with the increasing steric repulsions. Inspection of Table 3 reveals that the C1–C2 bond lengths calculated by MINDO/3 are invariably greater than those calculated by EFF, and that the difference (last column) increases almost linearly with the number of double bonds, each π system contributing roughly 0.006 Å to the bond lengthening. The residual bond lengthening (0.026 Å) indicated in Table 3 for octahydro-PDB typifies a general trend: MINDO/3 C–C single bond lengths in this class of compounds are

Table 3. C1–C2 bond lengths (Å) of PDB and hydrogenated derivatives

Compound[a]	Symmetry	EFF	MINDO/3	(MINDO/3)-(EFF)
PDB	D_{2h}	1.543	1.595	0.052
Dihydro-PDB	C_s	1.546	1.591	0.045
5,6,7,8 - Tetrahydro-PDB	C_{2v}	1.549	1.591	0.042
5,8,10,11 - Tetrahydro-PDB	C_{2h}	1.549	1.589	0.040
5,8,9,12 - Tetrahydro-PDB	C_{2v}	1.551	1.590	0.039
Hexahydro-PDB	C_s	1.555	1.588	0.033
Octahydro-PDB	D_{2h}	1.560	1.586	0.026

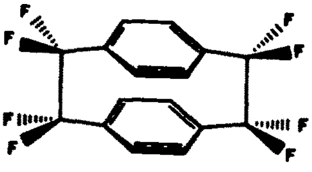
[a] Numbering as in Figure 1.

generally longer (by *ca.* 0.02 Å) than the EFF bond lengths.

Substituent effects. When viewed in terms of the top-bottom PMO analysis, the effect of substituents on PDB is expected to reflect the effect of substituents on the benzene-like fragments, and therefore on benzene itself. To study these effects, the following groups were placed on the 5 position using standard geometries for the substituents and the MINDO/3 optimized geometry for PDB: methoxy (Me group s-*cis* or s-*trans* to the C5–C8 bond), hydroxy (hydrogen s-*trans* or *exo*-perpendicular to the C5–C8 bond), ethyl (Me group s-*cis* or s-*trans*), nitro (coplanar with C5–C8) and cyano.

To gauge the effect of a particular substituent on the bond length, the force (negative of the derivative of the energy with respect to a change in bond length) on the C1–C2 bond length was calculated by MINDO/3. Table 4 summarizes the salient results. All substituents give rise to a positive force, indicative of bond lengthening. The OH group with the O–H bond *exo*-perpendicular to the C5–C8 bond still produces a significant force, even though π donation is presumably ineffective. This suggests that σ effects may be operative. The fact that the largest force arises from the s-*cis* Et group emphasizes that steric effects may be of major significance. In the case of 5,6,7,8-tetrahydroxy-PDB (all s-*trans*) the force on the C1–C2 bond is roughly double that for 5-hydroxy-PDB (s-*trans*), indicating that the effects are approximately additive for substituents placed vicinal to the C1–C2 and C3–C4 bonds.

Effects of substitution at the 1–4 bridgehead positions of PDB were studied on 1,2,3,4-tetrafluoro-PDB (3). A MINDO/3 geometry optimization (D_{2h} symmetry assumed, all C–H bonds fixed) yields a structure with a C1–C2 bond length of 1.581 Å, shorter than that of PDB. It is known that fluorine substitution significantly lowers the energy of the substituted C–C bonds,[18] and that this effect turns off through-bond coupling in octafluoro-[2,2]paracyclophane[19] (4) relative to [2,2]paracyclophane.



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The shorter bond length in 3 is in harmony with the expected diminution in through-bond interactions. Although this conclusion should be regarded with some caution, since MINDO/3 is known[9b] to underestimate the lengths of C–C bonds adjacent to F atoms, we note that replacement of H1–H4 of PDB (MINDO/3 geometry) by four fluorines (C–F = 1.40 Å) leads to a significant increase in the EHT C1–C2 overlap population relative to PDB, a result which also suggests a decrease in through-bond coupling in 3.

Extensions

Apart from lepidopterene and the various benzenoid dimers discussed previously,[4] several other classes of compounds have been studied for which a significant amount of bond lengthening due to through-bond coupling is expected. Several examples are presented here. The dimer of 5,6,7,8-tetrahydro-2-quinolone[20] (5) has a structure very similar to PDB and a C1–C8' bond length of 1.623 Å, with valence angles around C1 and C8' of relatively normal magnitude (e.g., C1–C8'–C7' = 112.2°, C1–C8'–C9' = 112.0°). It is likely that the observed bond

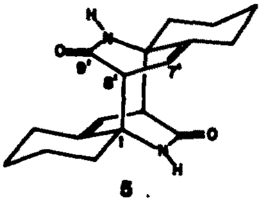

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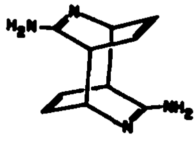
Table 4. MINDO/3 forces in substituted PDB's

Substituent[a]	Force[b]
Methoxy (s-cis)	12.87
Methoxy (s-trans)	4.30
Hydroxy (s-trans)	2.56
Hydroxy (exo-perpendicular)	1.73
Ethyl (s-cis)	15.11
Ethyl (s-trans)	12.29
Nitro (co-planar)	1.91
Cyano	8.50
5,6,7,8-Tetrahydroxy (all s-trans)	4.90
1,2,3,4-Tetrafluoro	- 7.71

[a] Unless otherwise specified, substituents are on the 5 position. Conformational descriptors are relative to the C5-C8 bond. See Figure 1.

[b] Force on the C1-C2 bond (kcal/mol-Å).

lengthening is the result of through-bond coupling, and the magnitude of the effect suggests that the amido groups participate effectively in these interactions. Long central bonds might also be expected in the photodimers of 2-aminopyridine (6)[21] and N - methyl - 2 - pyridone (7),[22] as a result of similar interactions.



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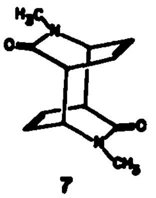

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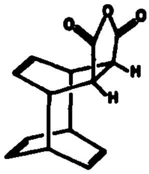
Compounds of the PDB type containing three π systems, and for which central bond lengthening might be expected, include 1 (although one of the oxygen lone pairs could also be involved), and 8.[23] *Syn*- and *anti-o,o'*-dibenzene[5] are prototypes for bond-lengthening involving two π systems. Particularly intriguing is the possibility for through-bond coupling in the class of pyrimidine dimers. The UV photodimerization of pyrimidines is one of the reactions which gives rise to mutagenesis in microorganisms,[24] and much interest has been expressed in the molecular structures of such dimers. It is therefore noteworthy that the dimers of 1,3-dimethylthymine (9),[25] uracil (10)[26] and methyl orotate (11)[27] all possess long central C–C bonds.



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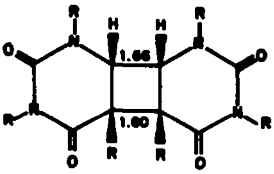
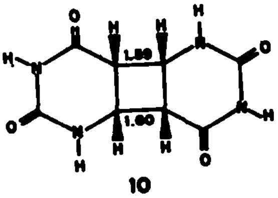


$R = CH_3$

9



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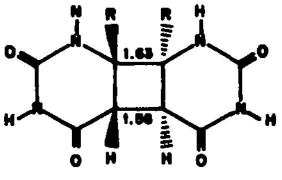

$R = CO_2CH_3$

11

This bond-lengthening may be taken as *prima facie* evidence for through-bond interactions between the N–C(O)–N–C(O) π systems. Although cyclobutane bonds naturally tend to be longer than normal C–C bonds, and although the substituents in 9–11 are forced to be nearly eclipsed, thereby increasing steric repulsions, the magnitude of the bond-lengthening, particularly in 9, is such that factors other than mere steric effects are likely to be operative.

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