

π -Electron Delocalization in Organic Molecules with C–N Bonds

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Most organic chemists are well acquainted with the concepts of molecular orbital theory and the notion that the delocalization of π -electrons frequently, but not always, leads to formation of a more electronically stable system. However, in the absence of evidence to the contrary, organic chemists often assume that if the delocalization of π -electrons in a conjugated π -system is possible and does not lead to anti-aromaticity, then delocalization must occur. This assumption is especially rigidly adhered to in discussions of molecules having the structural features that would allow them to obey Hückel's rules for aromaticity. These molecules are automatically assumed to be aromatic, notwithstanding the many examples of molecules that possess the structural features required by Hückel's rules but are not aromatic (1–3).

Obviously, organic chemistry would benefit considerably if we were to begin our discussions on π -systems with the phrase (encountered in most discussions of molecular orbital theory) "...if the π -system is delocalized, then...". However, nearly all our current textbooks on organic chemistry embrace the delocalization assumption above, and so teachers and students of organic chemistry rarely, if ever, encounter a discussion of delocalization in the ground states of π -systems.

This work did not seek to cast doubt on the reality of delocalization in suitable conjugated π -systems, but rather to demonstrate that delocalization is not an obligatory phenomenon in conjugated molecules. This undergraduate research project involved the examination of a few simple molecules (using their X-ray crystallographic coordinate data) whose conjugated π -systems would normally be assumed to be delocalized, but which in fact are clearly not delocalized, as will be shown by the analysis of their bond lengths and dihedral angles.

The Significance of Bond Lengths

Although there are experimental methods for assessing the aromaticity of molecules and delocalization, X-ray crystallographic coordinate data have not been widely or easily used, especially in a pedagogical context. Recently, new, bond-length based criteria were advanced for the unambiguous assessment of the aromaticity of molecules that meet the structural requirements of Hückel's Rules (1–3). The new criteria also unambiguously assess the existence of π -electron delocalization in nonaromatic π -systems. The bond length criteria are shown in Table 1 (2, 3), along with the correlation of these bond lengths with their bond orders, as determined by VESCF-HMO calculations.

We can illustrate the new criteria by considering the bond lengths in benzene and cyclooctatetraene. The non-planar cyclooctatetraene molecule is an example of a non-delocalized, alternant, polyene in which delocalization would have significantly negative energetic consequences (anti-aromaticity). The C=C double bonds embrace dihedral

angles that cannot possibly allow delocalization, and have lengths of 133 pm, almost identical to that of ethene. The C–C single bonds have lengths of 148 pm, which though less than ethane's 154 pm, *must* be single bonds. The lengths of the C=C double bonds of cyclooctatetraene are therefore illustrative of non-delocalized double bonds, and this molecule clearly has two kinds of carbon–carbon bonds. On the other hand, the length of each carbon–carbon bond of benzene is 139 pm, showing that there is only one kind of carbon–carbon bond in benzene. Although we can write alternant polyene structures (canonical forms) for benzene, there are no carbon–carbon single bonds in benzene and the observed carbon–carbon bond lengths are close to, but significantly longer than, those of isolated C=C double bonds. The archetypal example of delocalization in benzene leads us to recognize that a truly delocalized π -system must be comprised only of delocalized multiple bonds, and that the alternant canonical structures of these truly delocalized π -systems are grossly inaccurate representations of these π -systems.

The molecular modeling criteria developed for use in detecting or confirming the existence of true delocalization (2, 3) are, simply, that the length of each truly delocalized bond in a π -system must be within the normal range of lengths of that type of multiple bond and greater than the length of a similar multiple bond in the simplest molecular example. For example, the length of the carbon–carbon bond is 133 pm in ethene and 139 pm in benzene, which is both within the stated (Table 1) range of lengths of all C=C bonds and toward the longer extreme of this range. All truly delocalized multiple bonds will satisfy similar criteria.

The bond length data needed to assess any π -system's aromaticity or delocalization should be obtained from the high resolution X-ray crystallographic, or other accurate, study of the relevant molecule's structure. Indeed, during the process of establishing these new criteria, the X-ray crystallographically determined coordinate data from several thousand organic molecules were examined and the correlation of the data with the postulate was almost per-

Table 1. Bond Type–Bond Length–Bond Order Relationships^a

Bond Type	Longest (pm)	Simplest (pm)	Shortest (pm)	Bond Order Range ^b	Numeric Type
C–C	164	153	142	< 1.5	1
C=C	142	133	125	1.5 to 2.5	2
C≡C	125	118	111	> 2.5	3
C–N	157	147	137	< 1.5	1
C=N	137	128	120	1.5 to 2.5	2
C≡N	120	116	107	> 2.5	3
C–O	153	143	133	< 1.5	1
C=O	133	124	117	1.5 to 2.5	2
C–S	201	188	175	< 1.5	1
C=S	175	164	154	1.5 to 2.5	2

^aThe simplest bond type was that in the smallest, structurally unperturbed molecule: e.g., the C–C bond of ethane and the C=C bond of ethene. The bond lengths are rounded values.

^bFrom VESCF-HMO calculations.

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fect. The exceptions proved to be from erroneous coordinate data or from low-resolution structural determinations that had relatively large experimental errors.

Ideally, the experimentally determined structural data of molecules, rather than data from theoretical calculations, should be used to assess delocalization in π -systems. However, there are many interesting molecules whose structures have not yet been determined by X-ray crystallography. Fortunately, most modern theoretical methods simulate the geometrical features of simple organic molecules with sufficient accuracy to allow us to confidently use the structural data of these models. We have therefore used bond length data from molecular mechanical and semiempirical studies to assess delocalization in molecules whose structures have not yet been determined by X-ray crystallography.

The examination of the lengths of the multiple bonds in the conjugated π -system of any molecule, in a search for the presence of delocalization, can be performed using any simple molecular modeling program. The only calculation involved is that of the distance between two atomic centers, using the classical equation from coordinate geometry

$$D = [(X_1 - X_2)^2 + (Y_1 - Y_2)^2 + (Z_1 - Z_2)^2]^{0.5}$$

Any errors in the calculated bond lengths must therefore be from errors in the coordinate data, which emphasizes the need to use accurately determined (high-resolution) coordinate data whenever possible. Thus, given orthogonalized coordinate data, this exercise can even be done manually by using a calculator. However, the process of manually examining each bond in a typical π -system would obviously be very tedious and time consuming, especially if many molecules were being studied.

Fortunately, the molecular modeling programs STR3DI.EXE (for MS-DOS) and STR3DIMW.EXE (for Microsoft Windows) can automatically perform these simple calculations, analyze the data, and then inform the user, both visually and textually, of the existence of delocalization in the target molecule (4). Like most, if not all, molecular modeling programs, STR3DI and STR3DIMW perform calculations in double precision math. The simplicity and elegance of the use of either of these molecular modeling programs allowed us to embark on a series of undergraduate research projects aimed at examining the involvement of nitrogen in delocalization in organic molecules. The exercises described herein have been performed using several other molecular modeling programs, which have provided the same results—although in a much more tedious fashion. This work outlines the development and execution of one undergraduate research project in delocalization.

An Undergraduate Research Project in Molecular Modeling

Delocalization involving the intra-annular C–N π -bonds of heterocyclic and heteroaromatic molecules had already been discussed as an undergraduate molecular modeling exercise (1), but delocalization involving extra-annular C–N π -bonds, and nitrogen lone pairs flanked by π -systems, had not been explored in this context. Thus, the mentor and the undergraduate researcher searched the literature together and selected several small molecules whose X-ray crystallographic structures had been determined.

The undergraduate was provided with the molecular modeling facilities, a computer running STR3DI.EXE or STR3DIMW.EXE. After brief training in the use of the program, the undergraduate was instructed to measure the bond lengths and dihedral angles that involved a nitrogen

atom in each molecule. Frequent consultations and exchanges of ideas then allowed us to focus attention on a small set of illustrative molecules and to plan the execution of the rest of the project, which is presented below. In essence, the mentor could choose to direct the project towards the examination of any of a number of molecular structural features. The project, only a part of which is presented here, was performed over a period of two semesters.

The C–N Bond

We examined the X-ray crystal structures of several molecules that had (i) a nitro group attached to an aromatic ring, (ii) an amino group attached to an aromatic ring, or (iii) an amino group attached to saturated carbon atoms or hydrogens; or (iv) satisfied all of these criteria.

The fourth group of molecules was particularly relevant, because the experimental error present in the data of any given molecule would be common to all bonds in that molecule. This would ensure an internally consistent set of bond-length data. All molecules that we studied provided results consistent with those discussed in detail herein. Space obviously limits the number of molecules that can be presented and we have chosen representative examples.

The Nitrobenzenes

Compounds 1 (5), 2 (6) and 3 to 5 (7) in Diagram 1 were representative of the first group of molecules, a set in which the nitro group was sterically prevented from becoming coplanar with the aromatic ring, so ensuring its inability to achieve delocalization between its π -system and that of the aromatic ring.

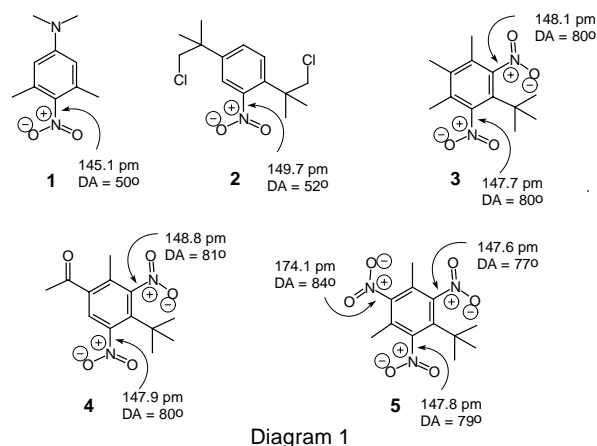


Diagram 1

In this group the lengths of the C–N bonds ranged from 145.1 to 149.7 pm, and the dihedral angles between the planes of the nitro group and the aryl ring, Diagram 1, confirmed the nonplanarity of the π -systems of these molecules. Notice that the lengths of the C–N bonds were not dependent on the dihedral angles and were also independent of the number of electron withdrawing groups on their rings, within the plausible experimental error of ± 2 pm.

In this study, the range of lengths of C–N bonds in the amino groups that were not flanked by π -systems, and so could not have delocalized lone pairs, was 145.6 to 151.4 pm. Thus, the lengths of the C–N bonds of the nitro-aryls above were identical to those of simple, non-anilinic (unconjugated) amines. Further, the lengths of the C–N bonds of many esters of 4-nitrobenzoic acid, and of uncrowded nitroalkanes, were also within the range 146.3 to 147.2 pm (with

nitrobenzoate dihedral angles randomly distributed in the range 2° to 12°), showing that the bond lengths present in compounds in this group were not due to sterically induced elongations.

These data lead to the unequivocal conclusion that these C–N bond lengths of nitro-aryls are typical of C–N single bonds and so they must be single bonds. Thus, there is no evidence for global delocalization of the π -systems of these simple nitro-aryl molecules in their ground states. The π -system of the nitro group is independent of that of the aryl group. In the language of molecular orbital theory, the resonance energy (stabilization) of the globally delocalized entity (which would necessarily be highly dipolar, with a positive charge in the aryl ring and a negative charge on the nitro group) must be less than the sum of the individual resonance energies of the two isolated π -systems (aryl and nitro groups), in these examples.

The chemistry and UV spectra of most simple nitro-aryls strongly indicate the presence of delocalization between the two π -systems. However, we have shown that this delocalization is not necessarily a normal feature of the ground states of these nitro-aryls. We must conclude that the process of delocalization that occurs during the reactions or photostimulations of the nitro-aryls must occur after these molecules are given sufficient activation (or electronic) energy to make delocalization favorable. Thus, during or before formation of the chemical transition or photochemically excited states of these nitro-aryls, these high-energy species do possess enough energy to make delocalization favorable.

These data and conclusions are further supported by data for the following set of molecules, which have three types of C–N bonds: from amino groups, nitro groups and the intramolecular heteroaromatic nitrogen of the quinoline system.

Localized and Delocalized C–N Bonds

The compounds **6** to **9** (**8**) in Diagram 2 are interesting because their bond length data are internally consistent with respect to experimental errors. Note the implied hydrogen bonds indicated by dashed lines.

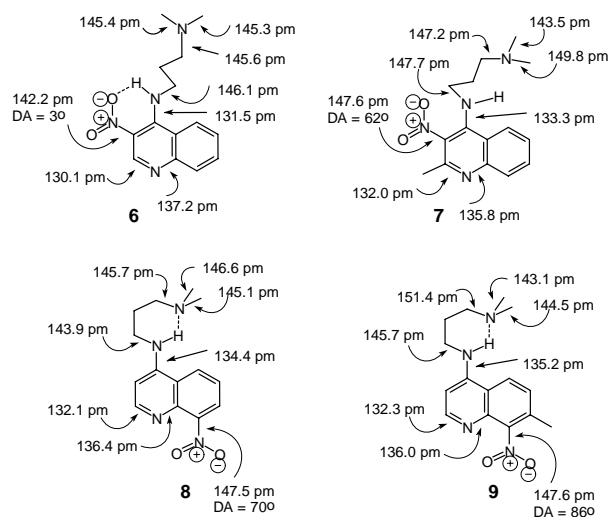


Diagram 2

For compounds **7** to **9**, the lengths the C–N bonds of the nitro groups (which were all greater than the limiting value of 137 pm, Table 1) showed that these bonds are single bonds. Indeed, these bond lengths were also quite similar to those of the C–N bonds of the aliphatic, non-anilinic,

amino groups. The nitro group's C–N bond in compound **6** was shorter than those of the other molecules in this set, but still within the range of lengths for single bonds (as it was greater than the 137 pm limit). This short single bond length was most likely due to the hydrogen bonding that was possible in compound **6** but not in the others.

The bond length data showed that the anilinic nitrogen possessed two types of C–N bonds. The length of the anilinic C–N bond was consistently within the range of lengths of the heteroaromatic C–N double bonds, revealing that the anilinic nitrogen's lone pair was truly delocalized into the quinoline π -system, and that the anilinic C–N bonds were really double bonds, rather than the single bonds normally used to depict these molecules. On the other hand, the "aliphatic" C–N bond of the anilinic nitrogen had the length of a normal C–N single bond, comparable with those of the other amino group's bonds.

The analysis above allowed us to determine, unequivocally, the true bonding features of these simple molecules by using only the bond length data derived from their experimentally determined coordinate data. This exercise was not easily performed heretofore and, as was seen above, it provided interesting and unexpected results.

Some Factors That Can Influence Anilinic Delocalization

Another intriguing study involved molecules whose π -systems bore both electron-withdrawing and electron-donating substituents. These electronic "push-pull" arrays are not always obvious candidates for intuitive analysis of the effectiveness of the "push" and "pull" factors, or their possible synergistic coupling, and so their overall bonding profiles are sometimes not clear. The study, described below, not only illustrates that unequivocal bonding profiles can be determined, but also further emphasizes the need for care in the "intuitive" analysis of the π -systems of conjugated molecules.

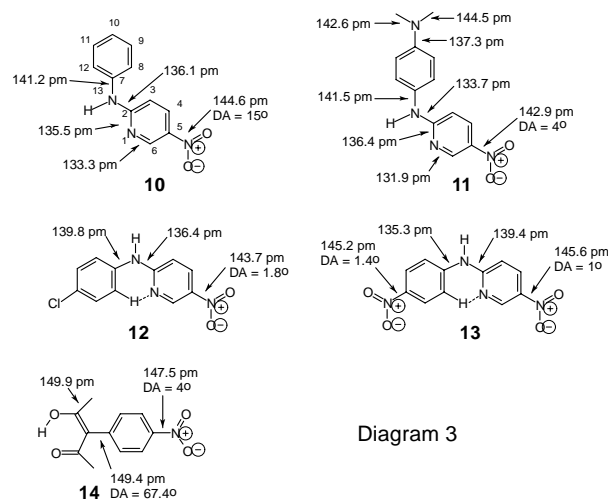


Diagram 3

All C–N bonds to nitro groups in compounds **10** to **13** (**9**) and **14** (**10**) were single bonds (with lengths greater than 140 pm). The dihedral angles with the pyridine ring varied from 1° to 15° , even though their intramolecular environments were identical, showing that these dihedral angles were determined by crystal packing forces only.

The lone pair of the anilinic *N,N*-dimethylamino group of compound **11** was delocalized into the benzenoid ring, as shown by the length of the resulting double bond, which was similar to the aromatic N-1–C-2 bond of the pyridine ring.

In compounds **10** to **13** the bonds to the anilinic nitrogen were clearly influenced by the substituent on the benzenoid ring. When this substituent was hydrogen or an electron-donating group, the N-13 lone pair was clearly delocalized into the pyridine ring. The stronger the electron-donating feature of the substituent, as in compound **11**, the more pronounced this effect seemed to be, as if the increased electron density in the benzenoid ring "pushed" the lone pair into the pyridine ring. In direct support of this analysis, in compound **10**, the 3-2-13-7 dihedral angle was 11° and the 2-13-7-8 dihedral angle was 33.5° , whereas in compound **11**, the 3-2-13-7 dihedral angle was 0° and the 2-13-7-8 dihedral angle was 48° . On the other hand, the electron-withdrawing benzenoid nitro group of compound **13** facilitated the delocalization of the N-13 lone pair into the benzenoid ring even though this nitro group was not directly involved in this process, since its C-N bond was still a single bond.

Compound **14** could also be considered to be a "push-pull" substituted system, but the electron-rich pentanedione moiety was not coplanar with the benzenoid ring and was attached to this ring by a single bond (same length as the C-CH₃ bond). Similarly, the nitro group was attached to the ring by a single bond. Thus, there were no push-pull interactions between these groups across the aryl ring.

We have seen strong evidence of trans-annular synergistic push-pull effects in other molecules, so we stress here that the absence of these interactions in these molecules does not allow us to conclude that these interactions do not exist. In a forthcoming paper, we shall show that subtle manipulations of bonding patterns by conformational and other factors are apparently of great significance in determining the biological properties of some molecules.

Delocalization Involving the Nitro Group

Notwithstanding the data above, we can find valid examples of the involvement of nitro groups in molecular delocalizations by looking at suitable high-energy species, such as the carbanions derived from nitroalkanes, but finding suitable examples in neutral molecules is obviously a challenge.

Of compounds **15** (*11*) and **16** to **18** (*12*), **15** served to remind us that amidic linkages are almost always delocalized (*2, 3*), except where geometrical restraints prevent it. Therefore compound **15** should best be represented by the structure **15A**. This was supported by the bond lengths.

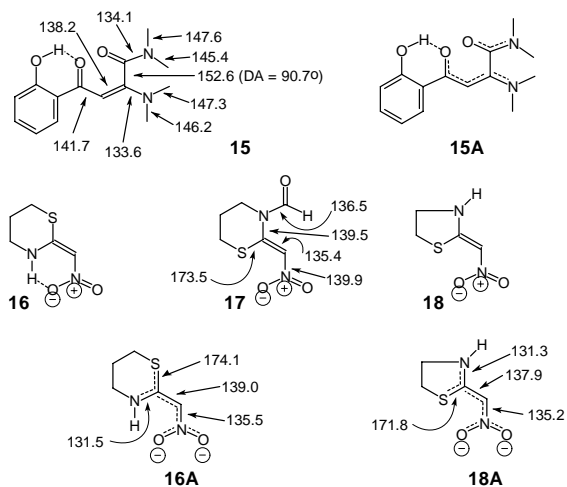


Diagram 4

Compound **16** should be represented by structure **16A**. Note that compound **17**, the *N*-formylated product of compound **16**, has essentially lost the delocalization involvement of the nitro group, since the C=C bond length was very close to that of an isolated (localized) C=C bond and the C-N length was that of a C-N single bond. The formyl group had, in effect, competed successfully for the (now amidic) nitrogen's lone pair.

Compound **18**, which is best represented as structure **18A**, showed that reducing the ring size from compound **16** did not affect the delocalization patterns. This might not be true when the ring size is reduced further and the 4-membered ring (thiazetane) analogue should show significant localization due to angle strain effects.

Project Conclusion

This study reminds us of the need to be very cautious when we encounter molecules in which two or more π -systems are conjugated. The almost involuntary rush to conclude that conjugated π -systems *must* be delocalized into one global π -system can lead to the wrong conclusion. In general, conjugated π -systems will form a globally delocalized entity only if the sum of the resonance energies of the isolated π -systems is less than the resonance energy of the globally delocalized entity. This comparison of resonance energies is not easily done, but the consequences of resonance energy differences can be readily appreciated in molecular modeling exercises similar to that described above.

Undergraduate Molecular Modeling

The data gathered in this undergraduate research project can obviously be used in many ways in the teaching of organic chemistry. Not only are the data very suitable for classroom discussions, but they are useful for designing and developing examination questions and quizzes. An entire "computer laboratory" class could rapidly examine selected molecules in a laboratory session, share the information after discussion, and write reports on their findings. As stated above, many aspects of molecular structure can form the bases for these exercises.

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