Nonbonded Interactions. The Influence of Lone Pair Repulsions on Bond Lengths

Gus J. Palenik, Anna E. Koziol, Alan R. Katritzky, and Wei-Qiang Fan
*Department of Chemistry, University of Florida, Gainesville, FL 32611, USA*

Nonbonded lone-pair repulsions are postulated as the cause of bond lengthening in isatin and a variety of other small molecules.

The influence of nonbonded interactions, either attractive or repulsive, on molecular structure is not well understood. In fact, unusual geometrical features in crystal structure studies are frequently attributed to 'crystal packing forces' or simply noted without further discussion. We report an example of carbon–carbon bond lengthening which can be attributed to nonbonded lone pair repulsions. The concept of nonbonded lone pair repulsions can be extended to explain long bonds found in other simple molecules.

The crystal structure of isatin had been determined and 'normal' carbon–carbon bond lengths were reported.[1] However, the refinement was limited by the computing
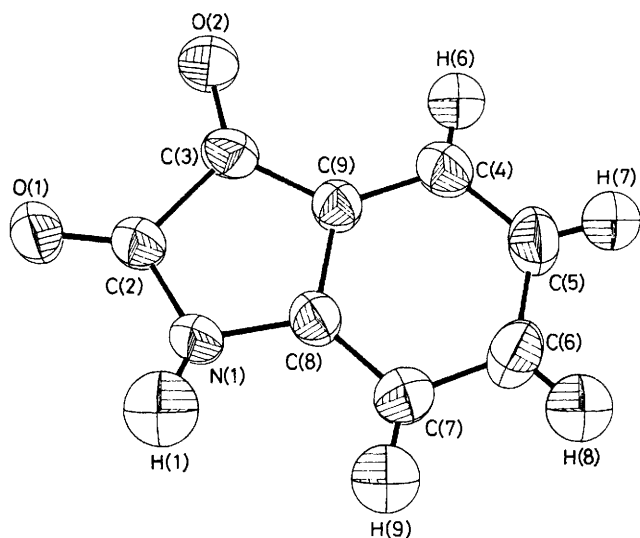
Figure 1. A view of the isatin molecule showing the 35% thermal ellipsoids and the atomic numbering. Pertinent distances are: N(1)–C(2), 1.352(3); C(2)–O(1), 1.220(3); C(2)–C(3), 1.555(3); C(3)–O(2), 1.213(3); C(3)–C(9), 1.455(3); C(9)–C(8), 1.402(3); C(9)–C(4), 1.381(3); C(4)–C(5), 1.375(4); C(5)–C(6), 1.387(4); C(6)–C(7), 1.383(4); C(7)–C(8), 1.368(3); C(8)–N(1), 1.402(3).

facilities available at that time. We have remeasured new intensity data and have refined the trial structure.† Our results have revealed an unusual and important feature of this molecule.

The structure of the isatin molecule is shown in Figure 1. The most striking feature is the very long C(2)–C(3) bond of 1.555(3) Å. This bond is significantly longer than the 1.48 Å

---

† *Crystal data*: $C_8H_5NO_2$, $M = 147.13$, monoclinic, space group $P2_1/c$, $a = 6.223(2)$, $b = 14.591(4)$, $c = 7.216(2)$ Å, $\beta = 94.42(3)°$, $U = 653.2(4)$ Å^3, $Z = 4$, $F(000) = 304$, $D_c = 1.472$ g cm^{-3}. A Syntex P1 diffractometer (upgraded to a Nicolet P3) was used to measure 857 reflections ($1.5 \leqslant 2\theta \leqslant 119.5°$) using Ni-filtered Cu-$K_\alpha$ radiation. The structure was solved using MULTAN80. Refinement of 744 reflections with $F_{obs} \geqslant 2\theta F_{obs}$ using anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for the hydrogen atoms converged to R 0.042 and R_w 0.033 with weights $= 1/\theta(F_{obs})^2$. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

---

expected for a $C(sp^2)$–$C(sp^2)$ single bond. Furthermore, any reasonable resonance structure which can be visualized would be expected to increase the double bond character of this bond and, consequently, an even shorter C–C distance would be predicted. A survey of *cis*-diketones found in the Cambridge Structural Database[2] (CSD) indicates that a long C–C bond distance [range from 1.506 to 1.582 Å, with an average of 1.542(17) Å for 43 values] is a common feature of these molecules. These molecules encompass a wide range of geometries, ring sizes, and substitutions so that the average value can be considered to be representative of a C–C bond in *cis*-diketones. In contrast the four *trans*-diketones found in the CSD file have a C–C bond distance which ranges from 1.418 to 1.504 Å, with an average of 1.476(27) Å. A simple explanation for these observations is that the lengthening in *cis*-diketones is caused by nonbonded lone pair–lone pair repulsions, not present in the *trans*-diketones.

The effect of nonbonded lone pair–lone pair repulsions can be used to explain the long bonds found in a variety of other molecules such as N_2O_4 (N–N 1.75 Å),[3] B_2F_4 (B–B 1.67 Å),[4] and oxalic acid (1.545 Å).[5] In all these cases there are *cis*-oxygen or -fluorine atoms which have lone pairs and a correspondingly long bond between the other atoms. In addition the easy decarboxylation of α-keto acids[6] can also be explained on the basis of a weakening of the C–C bond because of the lone pair–lone pair repulsion.

We thank the Center for Instructional Research Computing Activities, University of Florida, for a generous grant of computer time. Funds for the diffractometer were provided in part by the NSF Grant CHE 8316675.

References

1 G. H. Goldschmidt and F. J. Llewellyn, *Acta Crystallogr.*, 1950, **3**, 294.

2 There are 39 *cis*-diketones with a torsion angle between 0 and 20° in the January, 1988, release of the Cambridge Structural Database (see F. H. Allen, O. Kennard, and R. Taylor, *Acc. Chem. Res.*, 1983, **16**, 146). There are only 5 *trans*-diketones with a torsion angle between 160 and 180°. A more detailed analysis will be presented elsewhere.

3 D. W. Smith and K. J. Hedberg, *J. Chem. Phys.*, 1956, **25**, 1282.

4 L. Trefonas and W. N. Lipscomb, *J. Chem. Phys.*, 1958, **28**, 54.

5 There have been a number of structure determinations of oxalic acid and oxalates. The example given by Y. Wang, C. J. Tsai, W. L. Liu, and L. D. Calvert, *Acta Crystallogr.*, *Sect. B*, 1985, **41**, 131, is one of the latest and most accurate.

6 R. W. Hanson, *J. Chem. Educ.*, 1987, **64**, 591.