JOURNAL OF PHYSICAL ORGANIC CHEMISTRY, VOL. 10, 125–127 (1997)

IMBALANCE OF THE KEKULÉ STRUCTURES IN 2,4,6-TRIMETHOXY-*S*-TRIAZINE

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Low-temperature (100 K) x-ray diffraction studies and *ab initio* calculations show significant localization of the π-electron structure in 2,4,6-trimethoxy-*s*-triazine. Possible rationalizations for this observation are discussed. © 1997 by John Wiley & Sons, Ltd.

J. Phys. Org. Chem. **10**, 125–127 (1997) No. of Figures: 3 No. of Tables: 0 No. of References: 17

Keywords: Kekulé structures; π-electron structures; 2,4,6-trimethoxy-*s*-triazine

Received 8 April 1996; revised 6 October 1996; accepted 15 October 1996

INTRODUCTION

Like the most aromatic π-electron system, benzene, which contains six C—C bonds of equal length, *s*-triazine in the gaseous,[1] liquid[2] and crystalline[3] states has six C—N bonds of equal length. As we shall show, this typical structural feature of aromatic character is broken in the 2,4,6,-trimethoxy derivative, as shown by the x-ray structure[4] and in particular by low-temperature (100 K) x-ray measurements. This effect is also observed in 1,3,5-trimethoxybenzene.[5] The dearomatization of the benzene ring due to non-symmetrical substituents is clearly of potential interest in synthetic organic chemistry, since localization of the π-electrons can change the reactivity and other physical or chemical properties. The effect of alternation of the ring bond lengths is best characterized by the HOSE model,[6] which permits the estimation of relative Kekulé structure contributions. In our previous study on anisole,[7] it was shown that the methoxy group induces shortening of the adjacent ring C—C bond *cis* to the OMe group. A remarkable finding was that, although the estimated through-space interaction energy between the methoxy group and the ring was small (ca 5 kJ mol^{-1}), an effect of significant bond length alternation is propagated around the whole ring (the relative Kekulé structure contributions were 52·6:47·4). Since *s*-triazine contains more polar bonds, we might expect an even more enhanced effect of the methoxy substituent on the ring geometry in methoxy-*s*-triazine derivatives. This paper presents results for one such compound.

RESULTS AND DISCUSSION

Figure 1 shows the bond lengths of 1,3,5-trimethoxy-*s*-triazine, as determined by an x-ray diffraction experiment

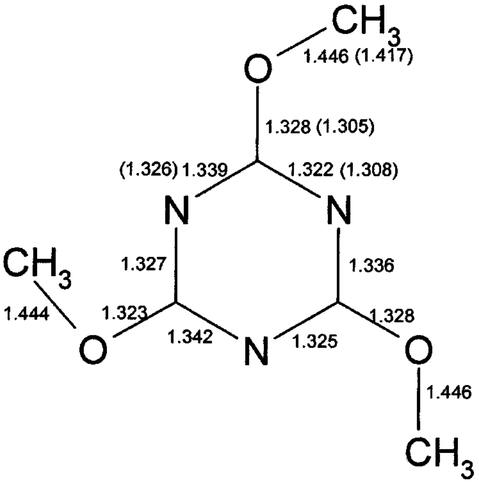

Figure 1. Low-temperature (100 K) bond lengths (*ab initio* values in parentheses) in 2,4,6-trimethoxy-*s*-triazine. Esd values from the covariance matrix for C—N bond lengths are typically 0·001 Å.

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Contract grant sponsor: Fundacja na Rzecz Nauki Polskeij; *Contract grant number:* BST-24/95.

CCC 0894–3230/97/020125–03 $17.50

carried out at 100 K [in parentheses are the values obtained from a Hartree–Fock 6–311G(d,p) *ab initio* optimization, imposing C_{3h} symmetry]. Within experimental error the ring is planar, and all three COCN dihedral angles are within a few degrees of zero. The crystal packing shows no short intermolecular contact. The CN bonds fall into two distinct groups: the three bonds *cis* to the methoxy group have a mean length of 1·324 ± 0·003 Å and the three bonds *trans* to the methoxy groups of 1·339 ± 0·003 Å. Here we have taken 0.003 Å as a more realistic estimate of the absolute experimental error on these bond lengths than the smaller values computed from the covariance matrix. The observed mean alternation of CN bond lengths is 0·015 ± 0·003 Å, which is still five times greater than this esd value. Moreover, it is in excellent agreement with the bond length alternation found in the *ab initio* calculation (0·018 Å). Figure 2 shows the two possible resonance structures, together with their relative contributions, computed using the HOSE model which requires only the bond lengths[7] (*ab initio* values in parentheses). An alternative measure of the π-electron delocalization (i.e. instead of the ring bond length alternation) is based on the electron distribution. The bond ellipticity measures the degree of double bond character using the two principal curvatures of the electron density perpendicular to the bond.[8] The two values obtained for the ring C—N bonds in 2,4,6-trimethoxy-*s*-triazine optimized at the 6–311G(d,p) level are 0.086 and 0.104, respectively.

In order to obtain independent information on how these subtle effects on ring geometry operate, we have also optimized the geometry of monomethoxy-*s*-triazine by *ab initio* 6–311G(d,p) calculations of the (lowest energy) planar and perpendicular conformations (i.e. methoxy group constrained to be perpendicular to the ring). In this way we estimated the interaction energy of the methoxy group with the ring from the associated barrier to rotation, which was found to be 32·2 kJ mol^{-1} (ignoring changes in stored vibrational energy). Based on the calculated bond lengths of the planar (lowest energy) structure, we derived HOSE-estimated Kekulé structure ratio of 54·5:45·5. In calculations where the COC bond angle, ϕ, is decreased from its optimum value (119·7°) by 5° and then 10° (the other geometrical parameters being optimized), this ratio changes to 55·9:44·1 and 57·5:42·5, respectively, as shown in Figure 3. Hence forcing the O—C bond of the methoxy group closer to the ring increases the π-electron localization, as evidenced by the C—N bond length alternation. If the Kekulé structure ratio is calculated *only* for bonds N–1—C–2—N–3. i.e. for the situation representing only local changes, then the appropriate ratios are 53·1:46·9, 54·9:45·1 and 57·1:42·9. The comparable effect observed in the closest vicinity of the methoxy group demonstrates that the whole ring is indeed responding to the perturbation. (Figure 3).

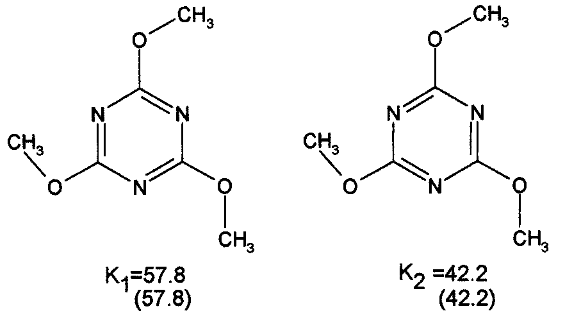

Figure 2. Resonance structures of 2,4,6-trimethoxy-*s*-triazine and their weights computed with HOSE (*ab initio* values in parentheses).

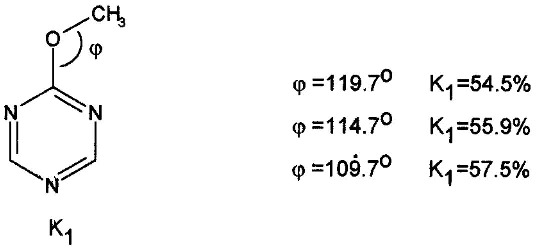

Figure 3. Changes in the resonance structure contributions of 2-methoxy-*s*-triazine due to the bending of the C—O—C angle (ϕ) by 5° and 10°.

Two conclusions may be drawn from the results presented above. First, the increased dearomatization shown by the difference in relative Kekulé structure weights for methoxy-*s*-triazine relative to anisole is consistent with the larger interaction energy found for the methoxy substituent and ring in the former case. The stronger interaction in the triazine derivative is apparently due to the presence of attractive intramolecular C—H· · ·N interactions. This could be seen as a weak bifurcated H-bond, although the contact distance of 2·67 Å is at the limit normally considered for such bonds.

Second, the results obtained may be interpreted in terms of the Hiberty–Shaik hypothesis[9, 10] that the so-called π-electron delocalization in the ring is a by-product of the σ-electron-imposed sixfold symmetry (of C—N bond lengths) and is not a driving force by itself. This subtle balance between σ- and π-electron contributions to the geometry of the ring is perturbed by interactions with the substituent group, leading to an increase of π-electron localization (bond alternation). Two kinds of effect may be operating here: (i) a weak through-space interaction and (ii) a through-bond interaction, such as the hyperconjugative effect discussed by Maulitz *et al*., who studied symmetrical triethyl derivatives of triazine and related compounds. Jug and Koester[12] showed that π-and σ-electron contributions to the total energy in 1,3,5-triazine are similar to those in benzene. Hence there is qualitative similarity of the results with those for anisole.[7] Further theoretical investigations into the nature of this bond length fixation are under way.[13]

EXPERIMENTAL

The x-ray structure determination at 100 K utilized equipment and techniques which have been described previously.[14] Refinement on the 1874 unique reflections with $F > 4\sigma(F)$ using SHELX-93[15] yielded an R value (based on F) of 0.0356 and a goodness of fit of 1.23. Further details of the crystal structure investigation may be obtained from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, quoting the full journal citation.

The Hartree–Fock geometry optimization calculations employed GAMESS[16] running on a DEC Alpha Risc workstation. The tolerance for optimization was set at 10^{-4} a.u. for the maximum force on any nucleus, and one third of this for the r.m.s. force. The ellipticity analysis of the charge distribution in the ring employed the AIMPAC programs.[17]

ACKNOWLEDGEMENTS

Financial support for T.M.K. (BST-24/95) and the use of a low-temperature device founded by Fundacja na Rzecz Nauki Polskiej are gratefully acknowledged. S.T.H. acknowledges the financial support of the Royal Society (UK) and the Polish Academy of Sciences.

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