

Mellitic Trianhydride, C₁₂O₉: The Aromatic Oxide of Carbon[†]

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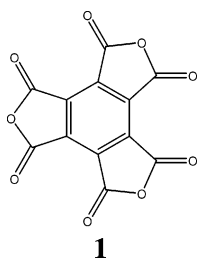
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Use of the ipsocentric method to map the pattern of current induced by a perpendicular magnetic field in the mellitic trianhydride molecule shows that, in addition to localized current associated with the carbonyl and oxygen centers, the field induces a strong central benzene-like ring current, thus indicating aromaticity on the magnetic criterion for this polycyclic oxide of carbon.

INTRODUCTION

A popular chemical brainteaser challenge might be to “name all the oxides of carbon”. In addition to the obvious answers of CO, CO₂, and C₃O₂, and discounting ions and the recent fullerene oxides C₆₀O¹, (C₆₀)₂O², and so forth, a well-established oxide that is often forgotten is mellitic trianhydride³ (MTA), which uniquely among well-characterized carbon oxides contains 50% of each element by weight. MTA has a polycyclic structure incorporating both carbocyclic and heterocyclic rings (**1**).



The parent hexacarboxylic acid (mellitic acid or graphitic acid) has been known for over 200 years, having been obtained from the unusual “organic” mineral mellite (honeystone, formula Al₂[C₆(COO)₆]·12H₂O) by Klaproth in 1799.⁴ Mellitic acid is also formed directly by the action of hot concentrated nitric acid on graphite.³ Synthesis of the trianhydride as a white, sublimable solid was announced in 1913 in a paper “On a New Carbon Oxide C₁₂O₉” by Meyer and Steiner.⁵ As was noted in the original paper, **1** forms highly colored (charge-transfer) complexes with various polycyclic hydrocarbons, and it is now known to be a powerful π acceptor.^{6,7} It has found applications in polymer science but has apparently attracted little attention from theoretical chemistry.

The molecular structure, as drawn, invites questions about the planarity of the structure. If the central carbon ring is benzenoid, and the nonbonded distances between the carbonyl groups are large, it would be expected that **1** would adopt *D*_{3h} symmetry. The crystal structure reveals “distinctly nonplanar” *D*₃-symmetric propeller-like molecules with dihedral angles of 4.9° between benzene and anhydride rings,

but this rather small deviation from *D*_{3h} symmetry is thought to arise from crystal-packing forces.⁸ Optimization of the geometry of the isolated molecule at semiempirical and RHF/STO-3G levels⁹ indeed leads to a planar, *D*_{3h} structure, and the MTA units in the crystalline 1:1 charge-transfer complexes of **1** with triphenylene and 9,10-dimethylantracene are found to be planar.⁸ An earlier study of the solid-state IR and Raman spectra¹⁰ of **1** had concluded that the observed frequencies could be consistently assigned using *D*_{3h} molecular symmetry, which may now perhaps be taken as another indicator that the in-crystal geometry is a result of weak perturbation of the “natural” *D*_{3h} symmetry of the molecular unit.

Another question about MTA relates to its putative aromaticity. Planarity would suggest that in MTA we are dealing with an aromatic molecule. Is the central ring of MTA benzenoid? The available evidence suggests that it is. The crystal structure determination was unable to resolve the two distinct bond lengths of the central hexagonal ring, owing to orientational disorder,⁸ but the only reported ab initio structure⁹ indicates a difference of only 0.001 Å between the central CC bonds exo and endo to the anhydride rings. Aromaticity can also be probed by checking whether a molecule sustains a ring current. Possession of a diatropic ring current is synonymous with aromaticity on the magnetic criterion.¹¹ As MTA has no H atoms attached to the central ring, an experimental detection of ring current through ¹H NMR chemical shifts is not possible, but the question can be approached theoretically, by calculating maps of induced current density, using the efficient, economical, and interpretable ipsocentric¹² method. That second approach is taken here.

CALCULATIONS

The geometry of MTA (**1**) was optimized at the RHF/6-31G** level in *D*_{3h} symmetry, and this symmetry was found to correspond to a true local minimum on the potential surface, with lowest vibrational frequency 58 cm⁻¹ (e⁻) and with bond lengths *R*_{CC(endo)} = 1.373 Å, *R*_{CC(exo)} = 1.392 Å, *R*_{CC(spoke)} = 1.498 Å, *R*_{CO} = 1.360 Å, and *R*_{C=O} = 1.167 Å. The equivalent crystallographically determined bond lengths⁸ are *R*_{CC(ring,average)} = 1.387 Å, *R*_{CC(spoke)} = 1.490(2) Å, *R*_{CO} = 1.396(2) Å, and *R*_{C=O} = 1.184 Å,

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[†] Dedicated to Professor Nenad Trinajstić on the occasion of his 70th birthday.

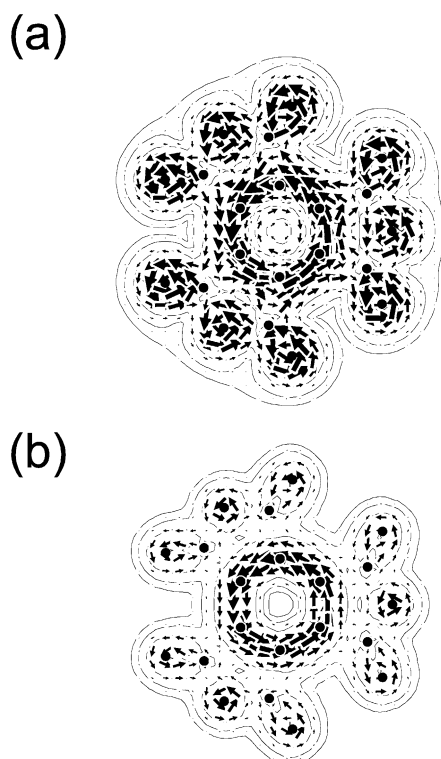


Figure 1. Map of induced current density in MTA. The magnetic field is directed along the symmetry axis, perpendicular to the plane of the figure, and the plotting plane is $1 a_0$ above that of the nuclei, with the arrows showing the projection of current density in the plotting plane and the contours showing its total magnitude, and anticlockwise circulations indicating diamagnetic/diatropic currents. Current density is calculated at the ipsocentric CT OCD-DZ/6-31G8//RHF/6-31G* level. (a) Total current arising from all ($\sigma + \pi$) orbitals and (b) contribution from the 12 occupied π orbitals of MTA.

respectively. Apparently, the D_3 propeller structure found in the crystal⁸ is not at a local minimum on the RHF/6-31G** potential energy surface for the isolated molecule: specimen D_3 structures produced by finite distortion from the RHF/6-31G** minimum all returned to the D_{3h} planar geometry upon relaxation. The RHF/6-31G* geometry retains planarity, with an indication of more bond alternation ($\Delta R = 0.019$ Å) than the reported⁹ minimal-basis STO-3G structure but consistent with the 0.007–0.014 Å spread of bond lengths in the central ring of MTA in crystalline complexes with triphenylene and 9,10-dimethylantracene.⁸

A calculation of the current density induced in the molecule by an external magnetic field directed along the 3-fold axis was then made in the same 6-31G** basis set at the coupled-Hartree–Fock CT OCD-DZ (“ipsocentric”)^{12–14} level of theory. The merits of this approach have been discussed extensively elsewhere:¹² it produces well-converged current-density maps in basis sets of modest size and gives a decomposition of total current in terms of orbital contributions that do not suffer from remixing in the presence of the field. Contributions from the occupied orbitals can be discussed in terms of canonical¹² or localized¹⁵ molecular orbital (MO) schemes.

The results of the calculations are shown in Figures 1–5, where current is mapped using our usual plotting conventions. In each case, the plotting plane is at $1 a_0$ above the plane of the nuclei, where π charge density and π current

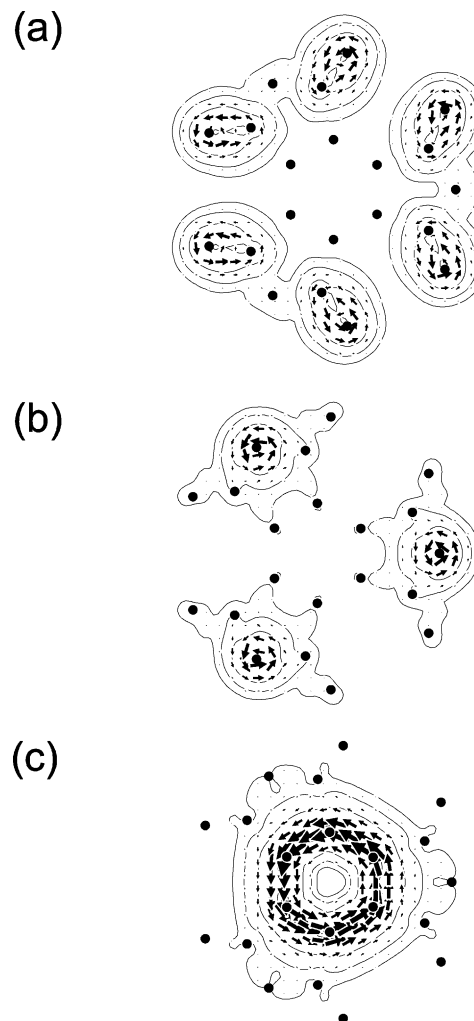


Figure 2. Orbital decomposition of current-density maps of MTA. Orbitals are localized according to the Pipek–Mezey criterion.¹⁶ The three panels of the figure represent the contributions of (a) the six carbonyl π bond functions, (b) the three lone pairs of the oxygen atoms of the anhydride rings, and (c) the three π orbitals of the central carbon ring of MTA. Plotting conventions are as in Figure 1.

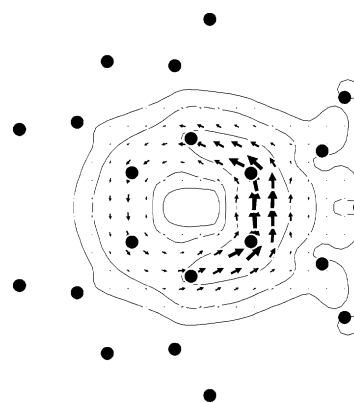


Figure 3. Current-density map showing the intrinsically delocalized nature of the π orbitals of the central ring of MTA. Pipek–Mezey¹⁶ localization of the occupied orbitals of D_{3h} -symmetric **1** yields three equivalent multicenter orbitals with open current flowlines. Only when all three are summed is a global closed-loop current recovered.

density are expected to be near maximal. Arrows show the projection of current density in that plane, and contours show

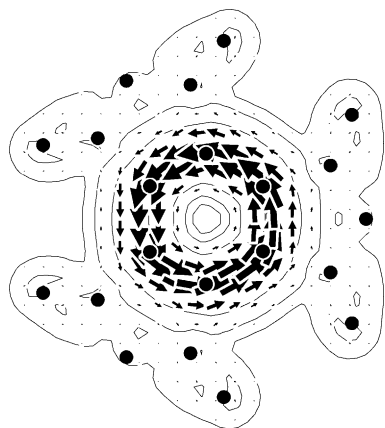


Figure 4. Current-density map showing the contribution of the four electrons of the $4e''$ orbitals (the “benzene HOMO” orbitals) of MTA. Plotting conventions as in Figure 1. The ring current can be attributed to four-electron diamagnetism, as in benzene itself.¹²

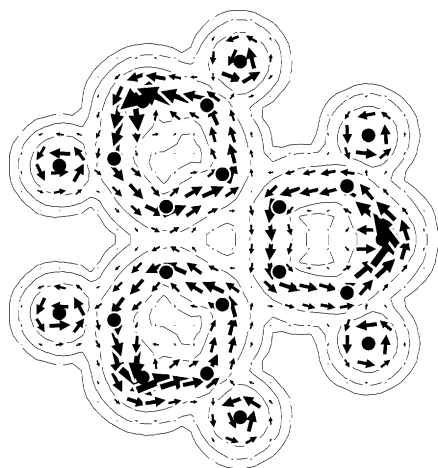


Figure 5. Current-density map of a model MTA^{6-} anion constructed by adding electrons to the molecule with the geometry frozen at that of the neutral. Plotting conventions are as in Figure 1. The map shows three furan-like diatropic ring currents in the anhydride rings in addition to local “lone-pair” eddies on the oxygen centers of the charged carbonyl groups.

its total magnitude. Anticlockwise circulations of arrows imply diamagnetic/diatropic currents.

RESULTS AND DISCUSSION

Figure 1a shows the composite pattern of current obtained when all orbitals ($\sigma + \pi$) are included in the calculation. When only those MOs of π symmetry are included (Figure 1b), the generalized diamagnetism of the σ framework is removed and the pattern breaks up into identifiable separate circulations—a circulation on the central ring and two sets of peripheral eddies on carbonyl and ring-oxygen groups. Further analysis into contributions from localized orbitals (defined by the Pipek–Mezey localization criterion¹⁶), as in Figure 2, shows the direct association between these currents and features of the electronic structure, through summation of contributions over the sets of equivalent orbitals. Specifically, the central circulation arises from a sum of three orbitals (Figure 3) that are spread over four carbon atoms, and separately each show the open pattern of current that is the signature¹⁵ of a (magnetically) intrinsically delocalized π system. The central circulation has the direction, magnitude, and uniformity of a true benzenoid ring current.

Evidently, the central ring current can be attributed to a locally delocalized electronic structure. A direct delocalized analysis of the central current is also possible: in terms of canonical orbitals, the central current arises essentially from a single orbital pair, the $4e''$ highest occupied molecular orbital (HOMO). This matches closely the pattern of the ring current in benzene itself, where in the ipsocentric account the whole current arises from the HOMO–LUMO (lowest unoccupied molecular orbital) virtual excitation.¹² When MTA is put into the context of “clamped” benzene systems,¹⁷ the survival of a central ring current is a sign that the essential topological structure of the benzene HOMO and LUMO are retained upon attachment of the anhydride rings, in spite of any bond alternation that they produce. Thus, it is correct to describe MTA as the aromatic oxide of carbon.

Finally, we note that, when electrons are added to the MTA system, the currents may be expected to show changes as old virtual excitations are blocked and new channels are opened. Figure 5 shows the effect of adding six electrons to MTA, neglecting any consequential changes in molecular geometry; the figure shows that this idealized hexa-anion is expected to exhibit three diatropic “furan” circulations, with extinction of the benzenoid character as the old HOMO–LUMO excitation channel is blocked by the extra electrons. This pattern of currents is compatible with a Lewis structure in which all six carbonyl oxygen centers bear a negative charge and the six CC “spokes” are double bonds, leaving the central ring devoid of double bonds; each five-membered ring then has a formal 6π electron count, arising from the two double bonds and an oxygen π lone pair. This hexa-anion too could be described as aromatic, but for reasons different from those that apply to the neutral molecule.

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