

## ORGANIC AND BIOLOGICAL CHEMISTRY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN, MADISON 6, WIS.]

New Aromatic Anions. III. Molecular Orbital Calculations on Oxygenated Anions<sup>1</sup>

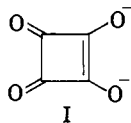
BY ROBERT WEST AND DAVID L. POWELL

RECEIVED FEBRUARY 22, 1963

Results from simple LCAO-MO calculations on anions of the  $C_nO_n^{-m}$  series correlate well with observed properties of known members of this group. Calculations have been carried out for a wide variety of possible anions with related but more complicated structures (Fig. 1). Most of these anions are predicted to have substantial resonance stabilization.

Previous communications have advanced our hypothesis that the cyclic anions  $C_nO_n^{-m}$  represent a new class of aromatic substances.<sup>1,2</sup> Evidence supporting this view is now available from a study of the vibrational spectra of the ions  $C_4O_4^{-2}$  and  $C_5O_5^{-2,3}$  which showed that these two ions do have the symmetrical planar structures suggested for them by earlier workers.<sup>4</sup>

In addition to the family of monocyclic anions  $C_nO_n^{-m}$ , related anions with more complicated structures may also prove to have aromatic properties. The Hückel LCAO-MO method has been used to calculate delocalization energies, bond orders, and charge densities not only for ions of the  $C_nO_n^{-m}$  series but also for a number of more complicated oxygenated organic ions related to these.<sup>5</sup> These calculations are all of the simple molecular orbital type and so are subject to the uncertainties well known to be associated with highly approximate calculations of this kind.<sup>6</sup> In particular, the delocalization energies cannot be compared quantitatively with those for more conventional aromatic compounds. In the hypothetical reference structures chosen for the calculation of the delocalization energies, the negative charges were localized on the oxygen atoms. Thus compound I was the localized



structure used in calculating the delocalization energy of diketocyclobutene dianion (structure III in Fig. 1). The choice of localized structures is arbitrary, but structures resembling I seem the most reasonable of the possible alternatives.

The coulomb and resonance integrals used in these calculations were mostly those recommended by Streitwieser.<sup>7</sup> Sample calculations using widely spaced param-

eters showed that the delocalization energies were relatively insensitive to the value chosen for these integrals. The general trends reported here are believed to hold for all reasonable choices of parameters.

Efforts were made to improve the calculations by the  $\omega$ -method<sup>10</sup> and, in a few cases, by SCF-MO methods; these were discontinued only when it was found that the results gave poorer agreement with experimental data than those of the simple unmodified calculations. More rigorous calculations would certainly be desirable, particularly for the highly symmetrical known species, but these might best be carried out after more complete structural information on the anions is available. In the meantime, the trends calculated by the simple MO method may have qualitative significance and predictive value within the class of compounds considered.

The results of the simple MO calculations, which were carried out with the aid of a high-speed digital computer, are shown in Fig. 1. The number given below each structure is the delocalization energy per  $\pi$ -electron ( $DE/\pi$ ), in units of  $\beta$ , for the total charge indicated. The quantity  $DE/\pi$  seems the best measure of delocalization to use when, as here, species with widely different numbers of  $\pi$ -electrons are to be compared. Atomic charge densities are indicated in Fig. 1 rather than free valence indices, which are of secondary interest for most of the anions treated. Calculated values for the  $\pi$ -bond orders are also shown.

**Monocyclic Anions,  $C_nO_n^{-m}$ .**—The anions now known among these species are  $C_4O_4^{-2}$ ,  $C_5O_5^{-2}$ ,  $C_6O_6^{-2}$ , and  $C_6O_6^{-4}$  (III-VII in Fig. 1). For the  $C_nO_n^{-2}$  series (compounds I-V, VII, and VIII)  $DE/\pi$  is substantial for all but the linear  $n = 2$  ion; it falls sharply from  $n = 3$  to  $n = 4$  and slowly with increasing ring size thereafter. These calculations are in agreement with experimental observations of the thermal stability of salts and of the acid dissociation constants of the parent enediols, which suggest a slight decrease in stability from III to IV to V. Alternation of resonance stabilization with ring size such as is found for the cyclic polyenes is neither predicted nor observed. Carbon-carbon bond orders are predicted to decrease, and carbon-oxygen bond orders to increase, as ring size increases. These predictions are in qualitative agreement with the results from normal coordinate analysis of the vibrational spectra of III and IV, but the predicted C-O bond orders are somewhat higher than those observed.<sup>3</sup> The unknown ion  $C_3O_3^{-2}$  is predicted to have an unusually high resonance energy, but angle strain, neglected in these calculations, may be expected to reduce the stability of this ion.<sup>11</sup>

while those in carbon-oxygen double bonds were given energies of  $\alpha + 1.4434\beta$ .

(8) G. Vincow and G. K. Fraenkel, *J. Chem. Phys.*, **34**, 1333 (1961).

(9) R. S. Mulliken, C. A. Rieke, and W. G. Brown, *J. Am. Chem. Soc.*, **63**, 41 (1941).

(10) A. Streitwieser, Jr., ref. 6, pp. 115-116.

(11) Ions with  $n > 6$  would also be strained and might undergo deformations from planarity to relieve this strain. Tentative indications from the infrared spectrum are that even the  $C_6O_6^{-2}$  ion may be slightly nonplanar in

(1) Previous paper in this series: R. West and H. Y. Niu, *J. Am. Chem. Soc.*, **84**, 1324 (1962).

(2) R. West, H. Y. Niu, D. L. Powell, and M. V. Evans, *ibid.*, **82**, 6204 (1960).

(3) M. Ito and R. West, *ibid.*, **85**, 2580 (1963).

(4) K. Yamada, N. Mizuno, and Y. Hirata, *Bull. Chem. Soc. Japan*, **31**, 543 (1958); S. Cohen, J. R. Lacher, and J. D. Park, *J. Am. Chem. Soc.*, **81**, 3480 (1959).

(5) The general name *oxocarbon* is suggested for substances of this class. The name is analogous to *fluorocarbon* and *cyanocarbon*, and refers to organic molecules or ions in which all, or nearly all, of the carbon atoms bear ketonic oxygen functions or their equivalents. In addition to ions of the types discussed in this paper, the name would also apply to such substances as leuconic acid,  $C_6O_6 \cdot 5H_2O$ , and triquinoyl octahydrate,  $C_6O_6 \cdot 8H_2O$ .

(6) J. D. Roberts, A. Streitwieser, Jr., and C. M. Regan, *J. Am. Chem. Soc.*, **74**, 4579 (1952); A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, pp. 97-101.

(7) A. Streitwieser, Jr., ref. 6, p. 135. The values used were  $k_{cc} = 1$ ,  $k_{co} = 0.8$ ,  $h_0 = 1$ . The value for the oxygen coulomb integral is close to that derived for the related semiquinone anions by studies of their e.s.r. spectra ( $h_0 = 1.2$ ); it was chosen so as to give reasonable charge separations. A resonance integral of  $0.7\beta$  was used for the C-C bond joining biaryl systems.<sup>9</sup>

In the localized structures,  $\pi$ -electrons in carbon-carbon double bonds and on negatively-charged oxygen atoms were assigned energies of  $\alpha + \beta$ ,

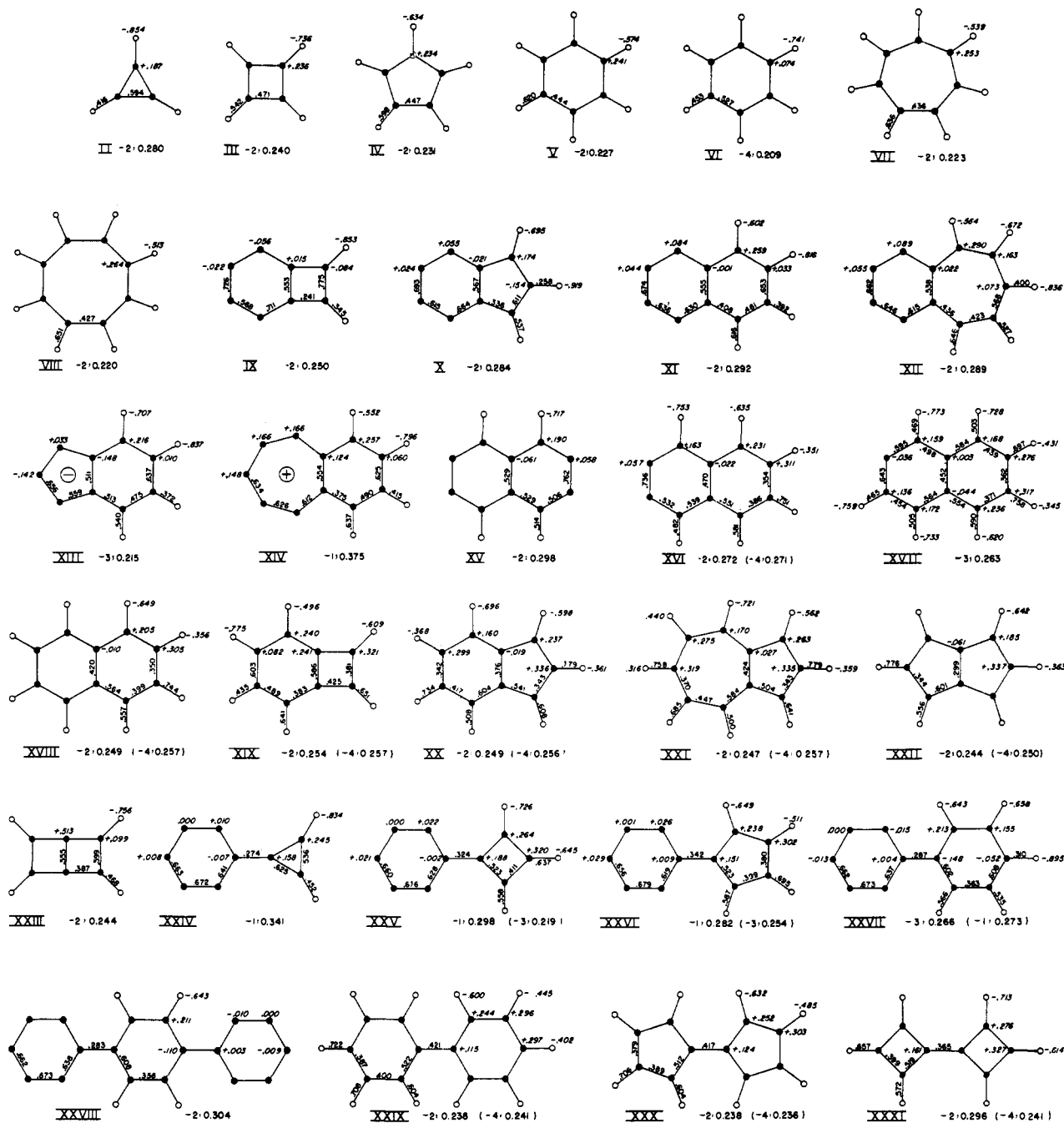


Fig. 1.—Results of LCAO-MO calculations on aromatic anions. The charge on the anion is shown below each diagram. Numbers with positive or negative sign indicate net charges on atoms, and unsigned numbers indicate  $\pi$ -bond orders. The delocalization energy per  $\pi$ -electron ( $DE/\pi$ ) is shown for each species; values given in parentheses are  $DE/\pi$  for anions of the same structure but of different charge, for which bond orders and atomic charges are not shown.

The energy levels for the ions  $C_3O_3^{-2}$  to  $C_8O_8^{-2}$  are shown in Fig. 2. The transition from the highest filled to the lowest unfilled level is allowed in each case, and is probably responsible for the prominent electronic absorption of III, IV, and V. A quantitative correlation is not expected, but the closer spacing of these levels with increasing ring size agrees qualitatively with the energies observed for the principal spectral transitions of the known ions (2500 Å. for  $C_4O_4^{-2}$ , 3630 Å. for  $C_5O_5^{-2}$ , and 4840 Å. for  $C_6O_6^{-2}$ ). The lowest unfilled orbital is degenerate in each of these ions and decreases in energy with increasing ring size. This level is calculated to be antibonding in II and III, but becomes bonding in IV and higher members of the series, which

the solid salt  $K_2C_6O_6$  (M. Ito and R. West, unpublished). Calculations show that the delocalization energy should not be greatly reduced by slight deviations from planarity.

suggests that anions of higher negative charge may be formed by the larger ring systems. These energy level calculations led directly to the successful synthesis of the tetrapotassium salt of the  $C_6O_6^{-4}$  ion VI.<sup>1</sup> Following Hund's rule, the two additional electrons might be expected to enter the degenerate level with parallel spin, to give a triplet state tetraanion. However,  $K_4C_6O_6$  was observed to be diamagnetic, perhaps because electron correlation effects neglected in our calculations operate to remove the degeneracy.<sup>1,12</sup>

Calculated  $DE/\pi$  values for  $C_nO_n$  species of different charge are shown in Fig. 3. Delocalization energies for ions of different charge are not strictly comparable, and the calculations are again not expected to have quantitative significance. However, the relative  $DE/\pi$  values

(12) Cf. D. P. Craig, *Proc. Roy. Soc. (London)*, **A203**, 498 (1950); A. D. Liehr, *Z. physik. Chem. (Frankfurt)*, **9**, 338 (1956).

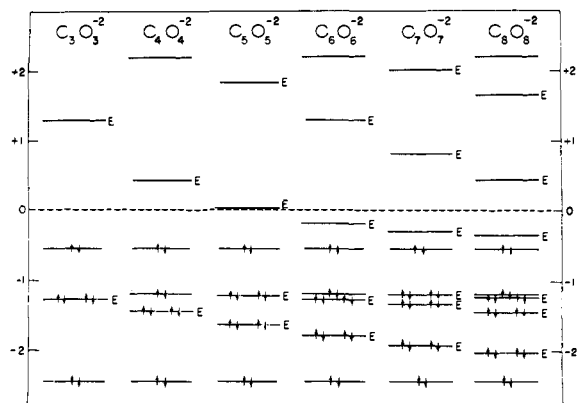


Fig. 2.—Energy levels for the  $C_nO_n^{-2}$  anions from  $n = 3$  to  $n = 8$ , from LCAO-MO calculations. Doubly degenerate levels are designated by the symbol E.

lead to the correct prediction that the  $-2$  ions are more stable than those of larger or smaller charge, at least for the smaller rings. A further prediction is that the dependence of stability on charge will be less marked as ring size increases.

**More Complex Anions.**—The remaining species in Fig. 1 (IX–XXXI) are typical examples chosen from the large number of more complicated anions for which calculations have been done. Almost all of these species are unknown as anions. A few are known in protonated form, and XVII and XXVIII are anions of known natural products. The listing is not exhaustive but is intended to indicate several of the more important types of oxygenated organic anions which may have considerable resonance stabilization.

Replacement of one or more oxygen atoms in a  $C_nO_n$  anion by other aromatic groups, thus lowering the symmetry, does not necessarily lower the predicted resonance stabilization. High values of  $DE/\pi$  are the general rule for the species in Fig. 1 and many of the more complex anions have higher values than those of the monocyclic  $C_nO_n^{-2}$  anions.

Species IX to XII have benzo groups fused to the oxocarbon ring in place of two of the oxygen atoms. All are predicted to have substantial resonance energy but IX, which is formally a derivative of cyclobutadiene, has a lower  $DE/\pi$  value than the others. As expected, the  $\pi$ -bond orders are generally greater in the conventional aromatic than in the oxygenated rings. Species XI is the dianion of 2,3-dihydroxy-1,4-naphthoquinone (isonaphthazarin). The disodium derivative of XI was first reported to be a blue solid by Bamberger,<sup>13</sup> but later described by other workers as yellow crystals.<sup>14</sup> The other anions in this group are unknown, but X may be present in the blue solution formed when hydrindantin is added to aqueous base.<sup>15</sup>

Other aromatic rings could presumably be substituted for benzene rings in species IX–XII; XIII and XIV show the effect of a cyclopentadienide and a tropenium ring, respectively. As might be predicted on qualitative grounds, stabilization is calculated to increase as the aromatic ring becomes more positive (XIV > XI > XIII). Species XV, the known dianion of naphthazarin,<sup>16</sup> has about the same value for  $DE/\pi$  as does its isomer XI. Species XVI–XVIII represent more highly oxygenated anions with the same skeleton; they are unknown, but the parent hydroxyquinones have been obtained for XVI and XVII. The latter is of special interest because, with appropriate alkyl substitution at

(13) E. Bamberger and M. Kitschelt, *Ber.*, **25**, 133 (1892).

(14) L. A. Shchukina, A. S. Khokhlov, and M. M. Shemyakin, *Zh. Obshch. Khim.*, **21**, 908, 917 (1951).

(15) S. Ruhemann, *J. Chem. Soc.*, **99**, 1306 (1911).

(16) Th. Zincke and M. Schmidt, *Ann.*, **286**, 27 (1895).

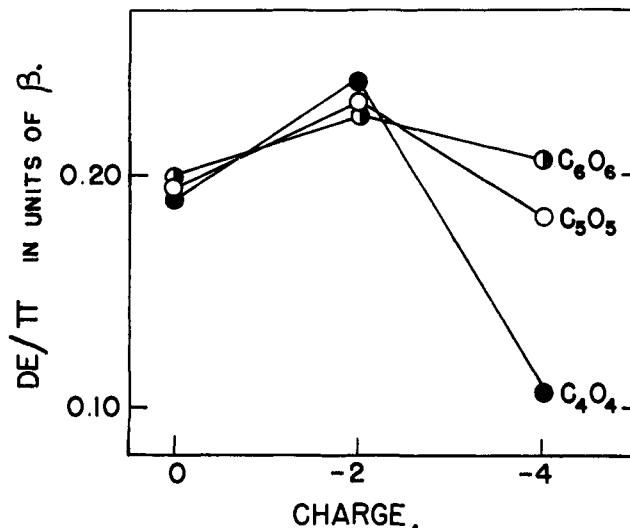
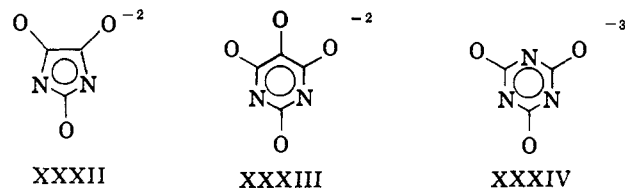


Fig. 3.—Delocalization energy per  $\pi$ -electron for  $C_nO_n^{-m}$  anions as a function of total charge.

the lone carbon atom which bears no oxygen, it represents the anionic form of natural pigments of the echinochrome and spinochrome series, found in the eggs and testes of sea urchins.<sup>17</sup> The anions XVIII through XXIII are all fused bicyclic oxocarbons; for charge  $-2$ ,  $DE/\pi$  is calculated to be essentially independent of ring size or symmetry. Examples are not shown, but fusion of a third or a fourth ring also gives anions with high predicted stabilization.

Substitution of a single oxygen atom by a phenyl group to give a "biaryl" system also gives anions with high  $DE/\pi$  values (XXIV–XXVII). These ring systems are unknown, but the disubstituted species XXVIII is the dianion of polyporic acid, the violet-brown pigment of the tree fungus *polyporus nidulans*.<sup>18</sup> Species XXIX–XXXI are examples of the many possible polyaromatic oxocarbons. Like the other classes of anions considered, they also are predicted to have high resonance energies, and the attachment of additional oxygenated rings also gives potentially stable anions.

Many possible heterocyclic ions related to this series could be considered. As an example  $>CO$  groups in these molecules might be replaced by  $>NH$ , as in the known compounds parabanic acid and alloxan. The dianions of these compounds apparently have not been studied. Using the parameters  $k_N = 1.5$ ,  $k_{CN} = 0.9$ ,



values of  $DE/\pi$  of  $0.208\beta$  and  $0.173\beta$  are calculated for the dianion of parabanic acid (XXXII) and alloxan (XXXIII), respectively. The same sort of delocalization is undoubtedly present in the trianion of cyanuric acid (XXXIV) which is calculated to have  $DE/\pi = 0.210$ .

**Acknowledgments.**—This research was supported in part by a grant from the National Science Foundation. Computations were carried out using the facilities of the University of Wisconsin Numerical Analysis Laboratory. The authors are grateful to the Dow Chemical Co. for a fellowship to D. L. P. and to Drs. Mitsuo Ito, L. C. Snyder, and H. J. Dauben for helpful discussions.

(17) Elsevier's "Encyclopedia of Organic Chemistry," Vol. 12B, 1952, pp. 3230–3238.

(18) P. R. Schildneck and R. Adams, *J. Am. Chem. Soc.*, **53**, 2377 (1931); F. Kögl, *Ann.*, **447**, 78 (1926).