

analytical reagents and novel inorganic ligands, which are currently inaccessible by known simple procedures, this phosphorus contraction reaction can be utilized. Extension of this work is now in progress.

Acknowledgment. We thank the National Science Foundation for partial financial support.

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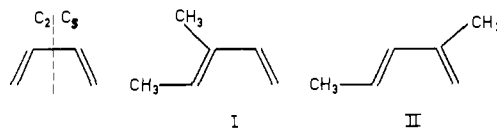
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Received April 10, 1978

True vs. Apparent Asymmetry

Sir:

We wish to show that the *electronic* asymmetry of a molecule may be strongly at variance with the visual *geometric* asymmetry which appears from simply looking at the molecule. By electronic asymmetry we mean the asymmetry of the total wave function, and of the measurable observables thereof (charge density, dipole moment, etc.). Consider the two substituted butadienes, 1,2-dimethylbutadiene (I) and 1,3-dimethylbutadiene (II), in their *cis* conformations. Relative to the two symmetry elements— C_2 axis, C plane—cutting through the midpoint of the central bond in the parent mole-



cule, I appears to be far more asymmetrical than II. We now proceed to show that the contrary is true for the full electronic ground states, and predict consequences which should be amenable to experimental verification.

It is convenient to consider first the changes in the individual molecular orbitals of butadiene brought about by the different substitution patterns. We consider, in the traditional manner, only the primary perturbing effect of the substituents: a change in Coulomb energy (the parameter α of Hückel theory) at the substituted carbon atom, with a concomitant change in the four π molecular orbitals. These four orbitals change by mixing with each other. We can write the new orbitals ψ_i in terms of the old ones ψ_j^0 ,

$$\psi_i = \sum_{j=1}^4 c_{ij} \psi_j^0$$

where the mixing coefficients, to first order, are

$$c_{ij} = 1 \quad (1)$$

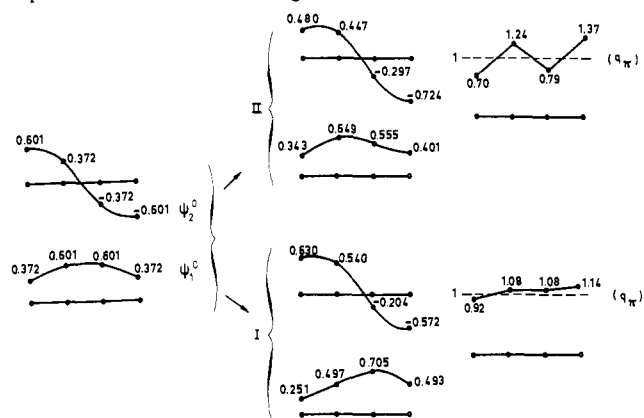
$$c_{ij} = \sum_{\text{perturbed centers, } r} \frac{c_{ir} c_{jr}^0}{E_i^0 - E_j^0} \Delta\alpha_r$$

In eq 1, $\Delta\alpha_r$ is the change in Coulomb integral at atom r , E_i^0 the energy of the i th orbital in the unperturbed molecule, and c_{ir}^0 the familiar LCAO expansion coefficients of this same molecular orbital.

The predominant induced mixing is determined by the substitution pattern. Large mixings occur between two MO's when the terms for the two substituted centers add in eq 1, i.e., when the products of the coefficients on the two substitution sites have the same sign in the two MO's. In I, ψ_1^0 mixes essentially with ψ_2^0 , and ψ_2^0 of course with ψ_1^0 (and slightly with ψ_3^0); in II, ψ_1^0 mixes exclusively with ψ_2^0 , and ψ_2^0 with ψ_3^0 . All of these mixings concern pairs of orbitals with different symmetry (A , S) and therefore contribute to the orbital asymmetry.¹ Scheme I shows the new molecular orbitals ψ_1 and ψ_2 (calculated for $\Delta\alpha = -\beta/2$) in molecules I and II.

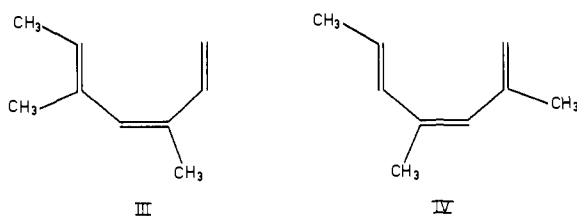
We now turn to the asymmetry of the *total* electronic ground state. Clearly any mixings between occupied orbitals will not change the overall π wave function or density (even though, as seen above, the individual orbitals are highly perturbed). Mixings between *occupied* and *unoccupied* orbitals, however, will affect this wave function.² Because of the important role of the energy gap between orbitals in determining the extent of mixing, the mixing between "frontier" orbitals

Scheme I. Change in the Occupied Molecular Orbitals of Butadiene upon Substitution. On the Right, Total Atomic π Densities



ψ_2^2 and ψ_3^2 gives the predominant contribution to the total electronic asymmetry. Examination of the product $\psi_2^2\psi_3^2$ at the substitution sites easily shows that molecule II (product with same sign on the two substituents) has a larger asymmetry than molecule I (different sign).

More generally, in an alternant hydrocarbon, the asymmetry will be largest if the substituted atoms all belong to the same set ("starred", or "unstarred").³ Two typical substitution patterns for hexatriene are shown, where molecule III has a small total asymmetry and molecule IV a large total asymmetry.



A first experimental test of these predictions can be made with the dipole moment. The calculated (ab initio, STO-3G) π -charge distribution⁴ and the π and total dipole-moment components are shown in Scheme II for the molecules in their equilibrium trans conformation. The calculated total dipole moments are mostly due to the π -system polarization. Furthermore, the contribution μ^π to the overall dipole is much larger in II than in I, whose dipole would be practically 0 were it not for the methyl contribution.⁵ The larger observed dipole in II vs. I (0.62 D vs. 0.58 D),⁶ although it confirms nicely our prediction of a larger electronic asymmetry in II, reflects only very partially the extent of the difference in electronic asymmetry.

Electronic asymmetry should also have a bearing on the rate of pericyclic reactions.⁷ For instance one might expect the concerted conrotatory motion to be slightly less facile in II than in I, or the disrotatory motion to have a slightly lower activation barrier. Preliminary calculations however do not seem to support this hypothesis, since no significant (>1 kcal/mol) activation energy difference is found in either process between I and II.

The asymmetry should also affect the *regioselectivity* of cycloadditions in which the asymmetric molecule is a partner. One might expect the regioselectivity to be greater the greater the electronic asymmetry. The regioselectivity of 1-methylbutadiene is larger than that of 2-methylbutadiene,⁸ in agreement with the larger total asymmetry induced by substitution at the C₁ atom (the mixing coefficient between ψ_2^2 and ψ_3^2 is larger in the 1-methyl compound). To our knowledge, the addition of dissymmetrical olefins to 1,2-disubstituted butadienes has not yet been studied, but the experimental obser-

vations on monosubstituted dienes⁸ indicate that the directing effects of the substituents should add in II and cancel in I, in agreement with the larger electronic asymmetry of II.

Acknowledgment. The authors are grateful to ATP No. 3328 for generous support.

References and Notes

- (1) Nothing forbids S,S or A,A mixings: for instance, for single substitution.
- (2) The same result is obtained by perturbation theory, which requires ground-state wave function to mix with excited wave function.
- (3) L. Salem, "The Molecular Orbital Theory of Conjugated Systems", W. A. Benjamin, New York, N.Y. 1966, p 36.
- (4) In both molecules, there is a slight incremental π charge, due to hyperconjugation, of 0.015 e⁻.
- (5) In the *anti*-1,2-dimethylbutadiene, the dipole moment is much smaller than in the *syn* isomer I (0.098 D vs. 0.258 D). Therefore, the dipole moment in I is mostly due to the *syn* orientation of the methyl groups.
- (6) These values are averages of gas phase and solution measurements: (a) N. B. Hannay and C. P. Smyth, *J. Am. Chem. Soc.*, **68**, 244 (1946); (b) E. H. Farmer and F. L. Warren, *J. Chem. Soc.*, 1302 (1933).
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Received May 10, 1978

Acoustic Emission during the Preparation of Dichloro(pyrazine)zinc(II)

Sir:

As part of an investigation on linear-chain compounds, having potentially bridging ligands, an unusual acoustic effect was noticed during the synthesis of the title compound. Upon addition of a solution of ZnCl₂ (1 mol/L) in water to a solution of pyrazine (1 mol/L) in water, immediately a precipitate is formed. This precipitation is accompanied by a rather strong cracking sound. This cracking is heard again when the mixture is shaken after some hours. The intensity of this acoustic emission appeared to be proportional to the concentrations of both the reactants; the higher the concentration, the louder the cracking. A temperature increase accompanies these crackings, which is stronger than the rise in temperature observed upon dilution of concentrated aqueous ZnCl₂ solutions.

In trying to understand this unusual effect, the reaction was carefully followed visually and it was noticed that, immediately after mixing, a very finely divided white-colored powder is formed, directly followed by the fast formation of bright white crystals, looking like a flash of lightning; the cracking is observed during this latter process.

The solid product has been analyzed by chemical analysis and IR and far-IR spectroscopy, and it was found that the compound is ZnCl₂pyr (pyr = pyrazine), identical with the compound prepared first by Stoehr.¹ However, the cracking was neither mentioned in this early report, nor in subsequent reports describing the spectroscopic properties and structure of this compound.² The IR and far-IR data of the final product are identical with those reported by other investigators.³ From these data it has been concluded that the Zn(II) ion can be considered as hexacoordinated, with an octahedrally based geometry in which both halide and pyrazine are bridging between the metal ions.

On searching the literature, no other examples were found that show a similar effect, making an explanation of this phenomenon very difficult and presently only some effects that may be responsible for the cracking can be suggested.^{4,6} A

Scheme II. Calculated π Charge Distribution and Dipole-Moment Components in Substituted Butadienes. The components μ^π have been calculated from the *point* π charges

