

of free radicals in Table II. In the corrected molecular orbital calculations, S was assumed to have the rounded-off value of 0.25. It is seen that the agreement of the various calculations with experiment and with each other is excellent in most cases, as is shown by the approximate constancy of the values of J , γ and β , and of the ratios J/β and β/γ . The discrepancies with butadiene (Table I) are presumably due to the fact that, with such a small effect, the complications arising from further factors, such as a lack of constancy of the integrals J , α , β , γ and S , the alterations in bond distances, etc., are relatively very important. The obviously impossible result that the resonance energy of cyclobutadiene is negative (Table I), which is obtained in the corrected molecular orbital calculation, is to be related to the fact, previously pointed out,⁶ that the molecular orbital treatment of this molecule does not take into account the resonance between the two Kekulé-like structures. With the free radicals (Table II) the calculated orders of increasing free radical resonance energy are in most cases the same as the observed order of increasing dissociation of the corresponding ethanes. While the valence bond treatment seems to reproduce the experimental order somewhat more satisfactorily in some regards than either of the molecular orbital treatments, there are too many further, unconsidered factors, such as solvent effects, entropy changes, steric effects, etc., to permit a judgment as to which of the three treatments is really the most accurate. This is especially true in view of the smallness of the differences involved. It is interesting that none of the methods accounts for the observed greater dissociating effect of the *m*-biphenyl group⁷ as compared with the phenyl group.

The conclusion to be reached from the above discussion is that, in cases like those considered, the explicit inclusion of the integral S in the molecular orbital treatment makes no significant difference in the self-consistency of the calculations of resonance energies of molecules, or of free radical resonance energies of radicals. There is no assurance, however, that the same will be true in the calculations of any other properties, especially in those cases in which the integrals α , β , γ and S cannot be considered constant. In fact, Mulliken and Rieke¹ have found that the

(6) G. W. Wheland, *Proc. Roy. Soc. (London)*, **A164**, 397 (1938).

(7) C. S. Marvel, E. Ginsberg and M. B. Mueller, *THIS JOURNAL*, **61**, 77 (1939).

explicit inclusion of S does materially improve the agreement of the calculations with the spectroscopic data. The fact that the value of the integral β is about twice that of γ also seems to be an improvement, since the old figure of $\gamma \cong -20$ kcal. per mole was hard to reconcile either with the known bond energies or with the ultraviolet absorption spectra of the molecules.

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NEW COMPOUNDS

α -Guanido- γ -methylmercaptobutyric Acid (Guanidomethionine)

The method employed for the preparation of this compound was similar to that reported for guanidocystine.^{1,2} To a solution of 0.74 g. of *dl*-methionine in 10 cc. of 0.5 *N* potassium hydroxide was added 1.04 g. of methyl-isothiourea hydriodide. The solution was put into a vacuum desiccator which was then evacuated for five hours. After a total of fourteen hours in the desiccator under reduced pressure the dried crystals were dissolved in 10 cc. of water. As before, this solution was slowly brought to dryness in the vacuum desiccator. The dried crystals were rubbed well with 30 cc. of acetone containing 6 drops of concentrated ammonia. Potassium iodide is soluble in acetone in the presence of ammonia. The crystals were filtered off, washed with two 5-cc. portions of ammoniacal acetone, then with plain acetone and air dried. The crude guanidomethionine was obtained as white crystals in about 92% yield. The Sakaguchi reaction was positive. After 3 recrystallizations from boiling water it was obtained as six-sided plates; dried in an Abderhalden apparatus, m. p. 193–194°.

Anal. Calcd. for $C_6H_{13}N_3SO_2$: N, 21.99. Found: N, 21.78.

(1) J. Kapfhammer and H. Müller, *Z. physiol. Chem.*, **225**, 1 (1934).

(2) Jesse P. Greenstein, *J. Biol. Chem.*, **112**, 35 (1935–1936).

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5-Iodo-7-bromoisatin and 2-Amino-3-bromo-5-iodobenzoic Acid

5-Iodo-7-bromoisatin.—A solution of 3 g. of 5-iodoisatin in 100 ml. of ethyl alcohol was heated to boiling under reflux and 5 g. of bromine added slowly. The reaction mixture was maintained at reflux temperature for eight hours, after which most of the alcohol was removed. The prod-