

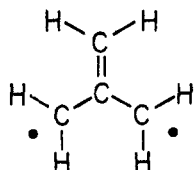
Zero Field Splitting Parameter of Trimethylenemethane

Avram Gold

Contribution from the Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138. Received April 1, 1969

Abstract: The zero field splitting parameter D is calculated for trimethylenemethane starting with single determinant and spin projected ($S = 1$) unrestricted Hartree-Fock wave functions. The results are compared to the value obtained for a limited configuration interaction calculation, and a positive value for D is suggested. The problem of good values for repulsion integrals in unrestricted wave functions is considered.

Since Hutchison's work on triplet naphthalene,¹ many theoretical calculations for zero field splitting parameters of triplet π -conjugated systems have appeared.²⁻¹⁰ Although a wide variety of systems has been treated, no detailed calculation has been done on trimethylenemethane (I).



I

Moreover, the sign of D in trimethylenemethane has been of some theoretical interest. McLachlan² and McConnell³ have both speculated on the effect on D of the large negative spin density predicted for the central carbon atom. McConnell suggested that D might be reduced to zero. McLachlan considered the possibility of a negative value for D and decided it was unlikely.

With the availability of the experimental epr spectrum of trimethylenemethane¹¹⁻¹³ and accurate values for atomic orbital dipolar interaction integrals,⁸ a calculation of D may be done for this molecule to compare theory with experiment.

McLachlan's limited configuration interaction (CI) treatment of trimethylenemethane² lacks only substitution of the proper values for the nearest and second nearest neighbor atomic orbital dipolar interaction integrals. Also, since no previous zero field splitting calculation has employed an unrestricted wave function, it seemed interesting to use an unrestricted Hartree-Fock (uhf) wave function and to compare the results with the completed CI treatment.

Wave Function and Spin Density

The uhf wave function for triplet trimethylenemethane is

- (1) C. A. Hutchison and B. W. Mangum, *J. Chem. Phys.*, **29**, 952 (1958).
- (2) A. D. McLachlan, *Mol. Phys.*, **5**, 51 (1961).
- (3) H. M. McConnell, *J. Chem. Phys.*, **35**, 1530 (1961).
- (4) R. McWeeny, *ibid.*, **34**, 399 (1961).
- (5) S. Boorstein and M. P. Gouterman, *ibid.*, **39**, 2442 (1963).
- (6) Y.-N. Chiu, *ibid.*, **39**, 2736 (1963).
- (7) J. H. van der Waals and G. ter Maten, *Mol. Phys.*, **8**, 301 (1964).
- (8) M. Godfrey, C. W. Kern, and M. Karplus, *J. Chem. Phys.*, **44**, 4459 (1966).
- (9) C. Thomson, *Mol. Phys.*, **10**, 309 (1966).
- (10) C. Thomson, *ibid.*, **11**, 197 (1966).
- (11) P. L. Dowd, *J. Am. Chem. Soc.*, **88**, 2587 (1966).
- (12) P. L. Dowd and K. Sachdev, *ibid.*, **89**, 715 (1967).
- (13) P. L. Dowd, A. Gold, and K. Sachdev, *ibid.*, **90**, 2715 (1968).

$$\Psi_T = \|\pi_1(1)\alpha(1)\pi_2(2)\beta(2)\pi_3(3)\alpha(3)\pi_4(4)\alpha(4)\| \quad (1)$$

π_1 and π_2 being the two bonding and π_3 and π_4 the two nonbonding molecular orbitals.

The self-consistent Hamiltonian matrix used for the orbitals of the α and β electrons is^{2,14}

$$F_{rs}^\alpha = \beta_{rs} - \delta_{rs} \sum_{t \neq l} \gamma_{rt} + \delta_{rs} \sum_l (P_{lt} + Q_{lt}) \gamma_{rt} - P_{rs} \gamma_{rs} \quad (2)$$

$$F_{rs}^\beta = \beta_{rs} - \delta_{rs} \sum_{t \neq l} \gamma_{rt} + \delta_{rs} \sum_l (P_{lt} + Q_{lt}) \gamma_{rt} - Q_{rs} \gamma_{rs}$$

where $P_{rs} = \sum_i a_{ri} a_{si}$ is the bond order matrix of the p α electrons, and $Q_{rs} = \sum_i b_{ri} b_{si}$ the bond order matrix of the q β electrons. The unpaired electrons are arbitrarily assigned α spin and the lowest p α orbitals and lowest q β orbitals obtained are used in the spin density calculations.

For the self-consistent field (SCF) calculation a geometry of 1.40 Å C-C bonds with 120° C-C-C angles was assumed. P and Q were initially formed from Hückel orbitals. Pariser-Parr values^{15,16} were used for the γ_{rs} , with $\beta_{rs} = -2.39$ eV for neighboring carbon atoms; $\beta_{rs} = 0$ otherwise.

It has been pointed out that the Pariser-Parr semi-empirical values for the repulsion integrals γ_{rs} are not correct for molecules in the triplet state.^{17,18} The Pariser-Parr γ_{rs} 's are estimated for doubly occupied restricted orbitals. Because of the singly occupied orbitals in the Pariser-Parr description of triplet molecules, the correction for electron correlation in the repulsion integrals must decrease. Use of singly occupied spin orbitals in the unrestricted wave function should make the necessary correction still smaller, so that larger values for the repulsion integrals should really be used. To test the effect of increasing γ_{rs} , the SCF calculations were also done using the theoretical values of γ_{rs} ,¹⁹ and the results are included in Tables I and II as footnotes.

The atomic orbital spin density at C_n , normalized to one electron total spin is given by

$$\rho_n = \frac{1}{2} \langle \Psi_T | \rho(r) | \Psi_T \rangle_{nn} \quad (3)$$

- (14) A. T. Amos, *Mol. Phys.*, **5**, 91 (1962).
- (15) R. Pariser and R. Parr, *J. Chem. Phys.*, **21**, 466 (1953).
- (16) R. Pariser and R. Parr, *ibid.*, **21**, 767 (1953).
- (17) K. Nishimoto, *Theoret. Chim. Acta*, **5**, 74 (1966).
- (18) K. Nishimoto, *ibid.*, **7**, 207 (1967).
- (19) R. Parr, D. P. Craig, and I. G. Ross, *J. Chem. Phys.*, **18**, 1561 (1950).

Table I. Spin Densities

Method	Peripheral ρ_p	Central ρ_c
Ψ_T^a	0.376	-0.128
$\Psi_T'^b$	0.354	-0.062
McLachlan limited CI ^{2,c}	0.314	-0.094
Complete CI ^{d,e}	0.388	-0.164
Experimental ^f	0.368	-0.104
Allyl, uhf, single detn ^{g,h}	0.651	-0.302
Allyl, uhf, $S = 1/2$ projected ^{g,h}	0.547	-0.093
Allyl, experimental ^g	0.581	-0.162

^a With theoretical γ_{rs} , $\rho_p = 0.411$, $P_c = -0.233$. ^b With theoretical γ_{rs} , $\rho_p = 0.380$, $\rho_c = -0.140$. ^c Restricted SCF molecular orbitals calculated with Pariser-Parr parameters. ^d Restricted SCF molecular orbitals calculated with Pariser-Parr values for γ_{rs} , $\beta_{rs} = S_{rs}W_p - \sum_{p \neq s} (rs|pp) + (p:rs)$. ^e J. A. Chapman and D. P. Chong, *Theoret. Chim. Acta*, **10**, 364 (1968). ^f An erroneous spin density has been published (footnote e) for trimethylenemethane. The expression for isotropic splitting, $a_H = Q\rho_p$, was used to estimate ρ_p . This relation is not correct for calculations on a single crystal. ^g L. C. Snyder and T. Amos, *J. Chem. Phys.*, **42**, 3670 (1965). ^h Pariser-Parr parameters.

Table II. Values of D

Method	D , cm ⁻¹
Ψ_T^a	-0.007
$\Psi_T'^b$	+0.044
McLachlan CI	+0.036
Experimental	0.025

^a With theoretical γ_{rs} , $D = -0.131$ cm⁻¹. ^b With theoretical γ_{rs} , $D = +0.028$ cm⁻¹.

where $\rho(r) = \sum_i 2S_z(i)\Delta(r_i - r)$ is the spin density operator. For the single determinant wave function, (3) reduces to

$$\rho_n = \frac{1}{2}(P - Q)_{nn} \quad (4)$$

The values obtained are given in Table I.

The unrestricted single determinant wave function is not an eigenfunction of S^2 . In calculating ρ_n and D , quantities dependent on spin distribution, the use of an eigenfunction of S^2 seems logical. Therefore the $S = 1$ state of Ψ_T was projected out and used in the zero field splitting calculation.

The projection operator for trimethylenemethane for spin state $S = 1$ is

$$O_1 = -\frac{1}{4}(S^2 - 6) \quad (5)$$

The wave function obtained by operating with O_1 was renormalized²⁰ to give the projected wave function

$$\begin{aligned} \Psi_T' = & 0.770 \|\pi_1(1)\alpha(1)\pi_2(2)\beta(2)\pi_3(3)\alpha(3)\pi_4(4)\alpha(4)\| - \\ & 0.257 \|\pi_1(1)\beta(1)\pi_2(2)\alpha(2)\pi_3(3)\alpha(3)\pi_4(4)\alpha(4)\| - \\ & 0.257 \|\pi_1(1)\alpha(1)\pi_2(2)\alpha(2)\pi_3(3)\beta(3)\pi_4(4)\alpha(4)\| - \\ & 0.257 \|\pi_1(1)\alpha(1)\pi_2(2)\alpha(2)\pi_3(3)\alpha(3)\pi_4(4)\beta(4)\| \quad (6) \end{aligned}$$

The atomic orbital spin density at C_n , normalized to one electron total spin, was calculated by (3) and the results are listed in Table I.

An experimental spin density was calculated using the hyperfine splitting constant from ref 13 and theoretically calculated hyperfine coupling tensors^{21,22} for the inter-

(20) T. Amos and L. C. Snyder *J. Chem. Phys.*, **41**, 1773 (1964).

action between a proton and the central and a adjacent peripheral spin densities. This result is also included in Table I.

Zero Field Splitting Parameter

The expectation value D (cm⁻¹) for the zero field splitting operator (\mathcal{D}) is given by^{28,29}

$$D = (3g^2\beta^2/2hca_0^2) \langle \Psi_T | \sum_{i < j} (r_{ij}^2 - 3z_{ij}^2) r_{ij}^{-5} \times (3S_z(i)S_z(j) - S(i) \cdot S(j)) | \Psi_T \rangle \quad (7)$$

For the single determinant Ψ_T with all spin orbitals mutually orthogonal, (7) reduces to

$$D = (3g^2\beta^2/4hca_0^2) \left[\sum_{i < j} \langle \pi_i(1)\pi_j(2) | (r_{12}^2 - 3z_{12}^2) r_{12}^{-5} | \pi_i(1)\pi_j(2) \rangle \mp \pi_i(1)\pi_j(2) \mp \pi_j(1)\pi_i(2) \right] \quad (8)$$

the top set of signs holding if π_i and π_j have like spins and the bottom set if π_i and π_j have opposite spins. When the π_i 's are expressed as linear combinations of atomic orbitals, $\pi_i = \sum_r \lambda_r a_{ri}$, D becomes

$$D = (3g^2\beta^2/4hca_0^2) \sum_{i < j} \sum_{r,s,t,u} (\pm a_{ri} a_{ti} a_{sj} a_{uj} \times \langle \lambda_r(1)\lambda_s(2) | (r_{12}^2 - 3z_{12}^2) r_{12}^{-5} | \lambda_t(1)\lambda_u(2) \rangle \mp a_{ri} a_{ui} a_{sj} a_{tj} \times \langle \lambda_r(1)\lambda_s(2) | (r_{12}^2 - 3z_{12}^2) r_{12}^{-5} | \lambda_u(1)\lambda_t(2) \rangle) \quad (9)$$

where $\langle \lambda_r(1)\lambda_s(2) | (r_{12}^2 - 3z_{12}^2) r_{12}^{-5} | \lambda_t(1)\lambda_u(2) \rangle$ are the atomic orbital dipole interaction integrals⁸ for Slater $2p\pi$ orbitals with $Z = 3.18$; C-C distance, 1.40 Å; and C-C-C bond angle, 120°. Evaluation of (9) is straightforward and the result is listed in Table II.

Evaluation of (7) for the projected wave function Ψ_T' is not nearly as simple. Since \mathcal{D} does not commute with O_1 , the entire linear combination of determinants must be used to find the expectation value of \mathcal{D} .²⁰

$$D = \langle \Psi_T' | \mathcal{D} | \Psi_T' \rangle \quad (10)$$

Furthermore, the spatial functions π_1 and π_2 are not orthogonal, so evaluation of \mathcal{D} between determinants in which π_1 and π_2 have like spins cannot be accomplished with expressions like (8). The expressions which must be evaluated are of the type

$$\langle u_i(1)u_j(2)u_n(3)u_m(4) | \mathcal{D} | \sum_P (-1)^P P u_i(1)u_j(2)u_k(3)u_l(4) \rangle \quad (11)$$

(21) H. M. McConnell and J. Strathdee, *Mol. Phys.*, **2**, 129 (1959).

(22) Hyperfine tensors calculated from the equations of ref 21 are very accurate when compared to available experimental data.²³⁻²⁷

The splitting between two lines of the hyperfine spectrum reported in ref 13 is given by

$$a_H = (A_p^p)_{zz}\rho_p + (A_c^p)_{zz}\rho_c$$

where $(A_p^p)_{zz} (= -69$ Mcps) and $(A_c^p)_{zz} (= -5.2$ Mcps) are the \hat{z} components (\hat{z} defined as the direction perpendicular to the molecular plane) of hyperfine coupling tensors for a proton with the spin densities on the peripheral adjacent and central carbon atoms. The requirement that total spin be normalized to 1 makes $\rho_c = 1 - 3\rho_p$, giving an equation for ρ_p . The sign of a_H is assumed to be negative.²⁸

The \hat{x} and \hat{y} principle values were not determined in ref 13. Therefore the usual method of estimating spin density²² $\rho_n = 1/3 \text{Tr}(\Sigma_i A_i^n)/Q$ cannot be employed.

(23) C. Heller and T. Cole, *J. Chem. Phys.*, **37**, 243 (1962).

(24) J. R. Morton and A. Horsfield, *Mol. Phys.*, **4**, 219 (1961).

(25) D. H. Whiffen, *ibid.*, **4**, 81 (1961).

(26) H. M. McConnell, C. Heller, T. Cole, and R. N. Fessenden, *J. Am. Chem. Soc.*, **82**, 766 (1960).

(27) H. J. Silverstone, D. E. Wood, and H. M. McConnell, *J. Chem. Phys.*, **41**, 2311 (1964).

(28) M. P. Gouterman, *ibid.*, **30**, 1369 (1959).

(29) M. Gouterman and W. Moffitt, *ibid.*, **30**, 1107 (1959).

where the u_i 's are spin orbitals, π_i , multiplied by the appropriate spin function. The result for D is listed in Table II.

McLachlan² reduced his limited CI treatment to the expression

$$D = 1.184\langle\lambda_1(1)\lambda_3(2)|(r_{12}^{-2} - 3z_{12}^2)r_{12}^{-5}|\lambda_1(1)\lambda_3(2)\rangle - 0.184\langle\lambda_1(1)\lambda_2(2)|(r_{12}^{-2} - 3z_{12}^2)r_{12}^{-5}|\lambda_1(1)\lambda_2(2)\rangle \quad (12)$$

Substitution of the correct values for the integrals yields D which is also listed in Table II.

Conclusion

For a large number of organic molecules, properties dependent on spin distribution have been calculated for single determinant and spin-projected single determinant wave functions. Projection usually results in better agreement with experiment.³⁰

Trimethylenemethane, like the allyl radical, has a central carbon atom with large negative spin density surrounded by peripheral carbons with positive spin. The single determinant unrestricted wave function considerably overestimates the negative central and positive peripheral spin densities in the allyl radical³⁰ (Table I). In the case of trimethylenemethane, comparison of the spin densities calculated from Ψ_T with those derived

(30) L. C. Snyder and T. Amos, *J. Chem. Phys.*, **42**, 3670 (1965).

from the hyperfine splitting indicates that the single determinant behaves in the same way, though less drastically. The large negative 1,2 spin correlation in trimethylenemethane would then be expected to result in a low value for D calculated from the single determinant.² Table II shows that this is true if the experimental D is positive.

D calculated for the projected wave function is positive and agrees well with McLachlan's value and reasonably well with the magnitude of experimental D . The agreement of D calculated with Ψ_T' with the result of McLachlan's limited CI calculation suggests that D is positive for trimethylenemethane.

Use of the larger theoretical repulsion integrals in the SCF calculation gives an interesting result. The positive peripheral and negative central spin densities of the projected wave function are enhanced (footnotes *a* and *b*, Table I) in the direction of the experimental values. This effect, as expected, decreases D slightly in the direction of the experimental magnitude (footnotes *a* and *b*, Table II). Perhaps a better estimate of the γ_{rs} for uhf wave functions would improve calculations of this kind on hydrocarbon triplets.

Acknowledgments. The author acknowledges helpful discussions with Professors M. Karplus and P. Dowd. The author also thanks Karen Gold for programming the SCF calculations.

Organometallic Electrochemistry. XIV.¹ The Conversion of Formal π Acceptors to π Donors

Raymond E. Dessy and Leonard Wiczorek

Contribution from the Department of Chemistry, Virginia Polytechnic Institute, Blacksburg, Virginia. Received February 6, 1969

Abstract: Infrared spectral data for a number of octahedral systems of the types $LM(CO)_6$ ($M = Cr, Mo$, and W ; $L =$ pyridine and quinoline), $L_2M(CO)_4$ ($M = Cr, Mo$, and W ; $L_2 =$ ethylenediamine, (pyridine)₂, and bipyridyl), $(LM(CO)_4)_2$ ($M = Cr, Mo$, and W ; $L = As(CH_3)_2$ and $P(CH_3)_2$), and $(LFe(CO)_5)_2$ ($L = SCH_3$, $P(CH_3)_2$, and $As(CH_3)_2$) before and after electrochemical reduction are presented. Force constants are calculated using the Cotton-Kraihanzel force field and the results discussed in terms of σ and π bonding.

Because of unique bonding of the carbon monoxide molecule^{2,3} in organometallic carbonyl compounds and its sensitivity to changes in electron density in the metal to which it is bonded, the infrared spectroscopy of these molecules in the carbonyl stretching region has been an extremely versatile tool.

The bonding between the carbon and oxygen atoms in a carbon monoxide molecule is comprised of a σ -bonding orbital and a pair of degenerate π -bonding orbitals. In addition, there exists a lone pair in non-bonding orbitals on both the oxygen and carbon atoms, the latter being the donor pair used in forming σ bonds with transition metals. The next lowest unoccupied

molecular orbitals are the doubly degenerate π -antibonding orbitals. The formation of the dative bond between the carbon monoxide and the (usually) low valence state metal results in a high charge density on the metal, a situation which is alleviated through the overlap of occupied d orbitals of correct symmetry on the metal with the π -antibonding orbitals of the carbon monoxide molecule. Occupancy of this antibonding orbital of CO results in a lower formal bond order between the carbon and oxygen atoms, and hence a lower C-O stretching frequency. It has also been shown that a change in σ charge density between the metal and CO directly affects the C-O stretching frequency.⁴

Therefore, in theory, by replacing one or more of the carbonyl groups with other ligands one can ascertain certain properties of these ligands as well as the bonding

(1) For previous papers in this series see R. E. Dessy, *et al.*, *J. Am. Chem. Soc.*, **88**, 453, 460, 467, 471, 5112, 5117, 5121, 5124, 5129, 5132, (1966); **90**, 1995, 2001, 2005 (1968).

(2) E. W. Abel, *Quart. Rev. (London)*, **17**, 133 (1963).

(3) G. Blyholder, *J. Phys. Chem.*, **68**, 2772 (1964).

(4) T. L. Brown and D. J. Darensbourg, *Inorg. Chem.*, **6**, 971 (1967).