

Self-Consistent Field Calculations of α - and β -Naphthol¹

Leslie S. Forster and Kichisuke Nishimoto

Contribution from the Department of Chemistry, University of Arizona, Tucson, Arizona, and the Mellon Institute, Pittsburgh, Pennsylvania.

Received November 2, 1964

The Pariser–Parr–Pople method (SCF formalism) is applied to the computation of transition energies and intensities and charge distributions in the ground and excited states of α - and β -naphthol. The calculated energy levels are in good agreement with experiment and fairly insensitive to the parameters employed. The transition intensities and charge distributions are sensitive to these parameters, but qualitative trends may be correctly predicted.

Introduction

In spite of serious theoretical shortcomings, the Hückel method has for many years provided a useful conceptual framework for the interpretation of diverse phenomena exhibited by π -electron systems.² This widespread usage of an admittedly defective method is an illustration of the oft-encountered principle that an imperfect theory is preferable to no theory at all. The availability of digital computers has made routine the calculation of orbital energies, electron densities, bond orders, etc., for molecules containing 30 (or more) π -electrons. The conceptual and computational simplicities of the Hückel method have been strong factors in its continued use and a comprehensive monograph² was published some 30 years after this approximation was introduced.

In the "simple" Hückel theory, electron repulsion is not introduced explicitly, but in 1953 this defect was removed without sacrifice of the intuitive appeal that characterized the Hückel scheme.³ In the intervening decade hundreds of papers concerned with the so-called Pariser–Parr–Pople method (or modifications thereof) have been published⁴ and a rather detailed description of the method has recently been included in a textbook.⁵ It is now evident that the computational and conceptual tools for such calculations are (or will soon be) available to a large number of workers.

The success of any semiempirical method depends upon the evaluation of suitable parameters, transferable from molecule to molecule. It is precisely in this respect that the Hückel method has failed when applied to π -electron systems containing heteroatoms. In this and succeeding papers we adopt a frankly pragmatic outlook in an attempt to determine suitable SCF parameters. When a sufficient number of studies of this type have been made, it will be possible to

judge the utility of the method and to delimit the domain in which it is applicable. It is particularly important to determine the effect of parameter variation on the energy levels and the π -electron distributions in the ground and excited states.

The naphthols are well suited for the evaluation of the effect of the –OH group on the properties of aromatic hydrocarbons as the transition energies and electronic distributions depend upon the position of the substituent.

Method

The self-consistent field (SCF) variant^{3b} of the Pariser–Parr–Pople method is well adapted for machine calculations, and all of the results described herein have been obtained by this technique. Similar calculations by the ASMO–CI method, the other commonly employed procedure, have been made for naphthalene and the naphthols.⁶ One purpose of this work is to compare the results of the two methods.

The notation and approximations employed have been previously described.⁷ One important difference must be noted, however. The expression for the core integral is

$$\alpha_p = -W_p - \sum_{q \neq p} N_q \gamma_{pq}$$

where $N_q = 2$ for the oxygen atom⁸ and 1 for the carbon atoms.

Ten iterations are sufficient to obtain convergence to ± 0.003 in the charge densities. The filled SCF molecular orbitals obtained are labeled ϕ_1 – ϕ_k (ϕ_1 is the highest filled orbital) while the unoccupied orbitals are designated $\phi_{1'}$ – ϕ_n ($\phi_{1'}$ is the lowest unoccupied orbital), where $2k$ is the number of π -electrons and $k + n$ is the number of atoms in the π -framework. The configurational functions Θ_m , for the one-electron excitations, $\phi_i \rightarrow \phi_j$ (ground-state orbitals are used for excited state configurations), are then used as a basis for a configuration interaction calculation. This CI calculation is made with a program that evaluates the resultant state energies and wave functions, E_a and $\Psi_a = \sum_m b_{am} \Theta_m$, as well as the intensities of the transitions $\Psi_a \leftarrow \Psi_0$ and the charge distributions in the excited states. A decision must be made regarding the number of configurations to be included in this calculation. Since we are primarily interested in the lower excited states, only configurations within 3 e.v. of the lowest excited configuration were included (this corresponds to an energy approximately 7 e.v. above the ground state). In the cases of α - and β -naphthol this encompasses 10 (or 11) of the 30 singly excited configurations.

(6) K. Nishimoto, *J. Phys. Chem.*, **67**, 1443 (1963).

(7) L. S. Forster, *J. Am. Chem. Soc.*, **86**, 3001 (1964).

(8) R. L. Miller, P. G. Lykos, and H. N. Schmeising, *ibid.*, **84**, 4623 (1962).

(1) Supported by the U. S. Atomic Energy Commission, Contract No. AT(11-1)-773 with the University of Arizona.

(2) A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961.

(3) (a) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466, 767 (1953); (b) J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953).

(4) An extensive bibliography is contained in R. G. Parr, "Quantum Theory of Molecular Electronic Structure," W. A. Benjamin, Inc., New York, N. Y., 1963.

(5) K. B. Wiberg, "Physical Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1964, pp. 108–122.

Table I. SCF Calculations of Naphthalene

Excited state	Excitation energy, e.v.			Oscillator strength (<i>f</i>)		
	Calcn. 1 ^a	Calcn. 2 ^b	Obsd. ^c	Calcn. 1	Calcn. 2	Obsd. ^c
¹ L _b	4.121	4.008	3.99	0	0	0.022
¹ L _a	4.269	4.287	4.51	0.191	0.270	0.11
¹ B _b	5.860	5.540	5.62	2.002	1.944	1.70
¹ B _a	6.274	6.178	...	0.981	0.852	...
³ L _a	2.773	2.343	2.64			

^a Theoretical γ_{pq} (nearest neighbor $\gamma_{CC} = 7.00$ e.v.). ^b Nishimoto and Mataga γ_{pq} ¹⁹ (equal bond lengths, $r_{CC} = 1.39$ Å.). ^c Reference 22.

Increasing this interval to 3.4 e.v. (15 configurations) is without appreciable effect on any of the transitions with energies < 6 e.v.

Geometry. The geometry of naphthalene⁹ was assumed to be unchanged upon substitution and the C–O distance was set at 1.39 Å.¹⁰ In α -naphthol, O₁₁ was placed in line with C₁ and C₄ while in β -naphthol, $\angle O_{11}-C_2-C_3 = 120^\circ$.

Parameter Choice. Assignments of the semiempirical parameters, W_p , β_{pq} , and γ_{pq} vary considerably. This is partly due to the relative insensitivity of the experimentally most accessible quantities, the transition energies, to the parameters utilized. If only transition energies are needed for spectral assignments, then this situation is favorable. If, however, properties involving wave functions (intensities, dipole moments, etc.) are to be calculated, it is quite likely that the choice of parameters will be more critical. This is one of the questions which we will examine below.

Valence State Ionization Energies, W_p . These quantities are set equal to 11.42 e.v. for all carbon atoms in naphthalene. For oxygen atoms donating two π -electrons, two very different values of W_O have been used, 34.95¹¹ and 23.5¹² e.v. The smaller value was used in the calculation of furan but in another study of the same molecule 34.16 e.v. was employed.¹³ We treat this quantity as a free parameter and determine the "best" value.

One-Center Repulsion Integrals. For carbon atoms, γ_{CC} is assigned as 10.84 e.v. (within the range, 10.53–11.13 e.v., generally used). Two values for the γ_{OO} integral have been suggested, 21.532¹⁴ and 16.86 e.v.,¹⁵ and both of these were used.

Two-Center Repulsion Integrals. The use of γ_{pq} calculated from theoretical formulas¹⁶ with adjusted exponents^{7,15} leads to an incorrect ordering of the two lowest excited states of naphthalene. Reducing the nearest-neighbor repulsion integrals by 0.8 e.v. ($\gamma_{CC} = 7.00$ e.v.), arbitrarily, corrects this problem. It has been shown that the differences in γ_{pq} are the important quantities rather than the values of individual integrals.¹⁷ The 0.8-e.v. reduction leads to differences in closer agreement with those suggested by Lykos.¹⁷

While several other prescriptions for the evaluation of γ_{pq} yield results not very different from those obtained with the Roothaan formulas,^{3a,18} a rather different set of γ_{pq} is obtained by the method of Nishimoto and Mataga.¹⁹ One aim of the present investigation is to compare the results obtained from these two sets of γ_{pq} which are designated theoretical and NM.

Resonance Integrals, β_{pq} . For carbon–carbon bonds ($r = 1.39$ Å.), $\beta_{CC} = -2.236$ e.v. has been used to fit the naphthalene spectrum.⁶ This quantity, somewhat smaller than the parameter commonly used (-2.40 e.v.), was obtained with the NM repulsion integrals. The naphthalene spectrum can also be fitted with the same β_{CC} and the theoretical integrals. The β_{CO} value is rather uncertain. For carbonyl C–O bonds ($r = 1.23$ Å.), $\beta_{CO} = -2.7$ e.v. has been used²⁰ and a much smaller value, -1.66 e.v., has been used for molecules with hydroxy substituents.²¹ We have employed an intermediate value, -2.115 e.v.,¹⁴ in most of the calculations but have varied this parameter over a wide range to evaluate the sensitivity of the results to this quantity.

Results and Discussion

Naphthalene. The naphthol results are to be compared with the naphthalene calculations. Two naphthalene calculations, differing only in the γ_{pq} integrals, have been made. These results are compared with experiment in Table I. Neither calculation is demonstrably superior to the other.

α - and β -Naphthol. The parameters used in the calculations are listed in Table II. In assessing the reliability of the SCF method and delimiting the domain of its applicability, we may use several criteria, in order of increasing stringency. At the lowest level, reasonable agreement between the observed and calculated transition energies is acceptable if the calculated transition energies are not too sensitive to parameter choice. This latter requirement minimizes the *ad hoc* character of the calculations and promotes the hope that the parameters may be transferable from molecule to molecule.

Singlet Transition Energies. In the weak sense outlined above, the calculated singlet state energies (Figures 1 and 2) are encouraging and these may be used for a preliminary screening of the parameters. The following points may be emphasized.

(9) S. C. Abrahams, J. M. Robertson, and J. G. White, *Acta Cryst.*, **2**, 238 (1949).

(10) H. C. Watson and A. Hargreaves, *ibid.*, **11**, 556 (1958).

(11) J. E. Bloor and F. Peradejordi, *Theoret. Chim. Acta*, **1**, 83 (1962).

(12) M. Orloff and D. Fitts, *J. Chem. Phys.*, **38**, 2334 (1963).

(13) D. Sappenfield and M. Kreevoy, *Tetrahedron Suppl.*, **2**, 157 (1963).

(14) K. Nishimoto and R. Fujishiro, *Bull. Chem. Soc. Japan*, **31**, 1036 (1958).

(15) L. Paolini, *Nuovo Cimento*, **4**, 410 (1956).

(16) C. C. J. Roothaan, *J. Chem. Phys.*, **19**, 1445 (1951).

(17) P. G. Lykos, *ibid.*, **35**, 1249 (1961).

(18) J. R. Hoyland and L. Goodman, *ibid.*, **36**, 12, 21 (1962).

(19) K. Nishimoto and N. Mataga, *Z. physik. Chem. (Frankfurt)*, **12**, 335 (1957).

(20) R. D. Brown and M. L. Heffernan, *Trans. Faraday Soc.*, **54**, 757 (1958).

(21) K. Nishimoto and R. Fujishiro, *Bull. Chem. Soc. Japan*, **37**, 1660 (1964).

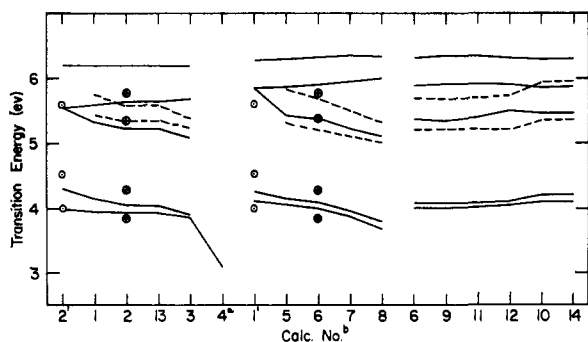


Figure 1. α -Naphthol singlet energy levels. — and - - - - - represent transitions likely to be observed and unobserved, respectively (see text). Experimental naphthalene and α -naphthol transitions are represented by O and \oplus , respectively: (a) no configuration interaction, only lowest configurational energy indicated; (b) 1' and 2' refer to naphthalene 1 and 2.

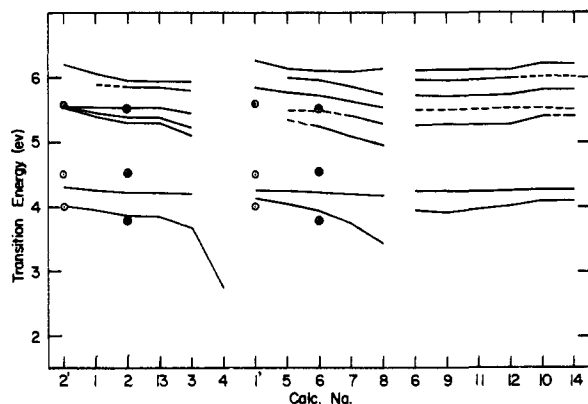


Figure 2. β -Naphthol singlet energy levels (same convention as in Figure 1).

(1) From calculations 1–4 and 5–8 the effect of varying W_O (NM and theoretical γ_{pq} are used, respectively, in the two sets of calculations) may be evaluated. The results are not too sensitive to W_O but it is clear that reducing this quantity below 30 e.v. leads to poor

Table II. Key to Calculations

Calc. no.	W_O , e.v.	γ_{OO} , e.v.	γ_{pq}^a	β_{CO} , e.v.
1	34.95	21.532	I	-2.115
2	33.00	21.532	I	-2.115
3	31.00	21.532	I	-2.115
4	23.50	21.532	I	-2.115
5	34.95	21.532	II	-2.115
6	33.00	21.532	II	-2.115
7	31.00	21.532	II	-2.115
8	29.00	21.532	II	-2.115
9	33.00	21.532	II	-2.400
10	33.00	16.860	II	-2.115
11	33.00	21.532	II'	-2.115
12	33.00	21.532	II'	-1.700
13	33.00	21.532	I'	-2.115
14	33.00	16.860	II'	-2.115

^a γ_{pq} values are designated as follows: I, Nishimoto and Mataga integrals¹⁹ ($r_{CO} = 1.39 \text{ \AA}$.); I', same as I for $r_{CO} = 1.46 \text{ \AA}$.; II, theoretical integrals, nearest-neighbor $\gamma_{CO} = 7.00 \text{ e.v.}$; II', same as II but nearest-neighbor γ_{CO} reduced by 0.8 e.v. All calculations with I and I' γ_{pq} are to be compared with naphthalene 2 and all others with naphthalene 1.

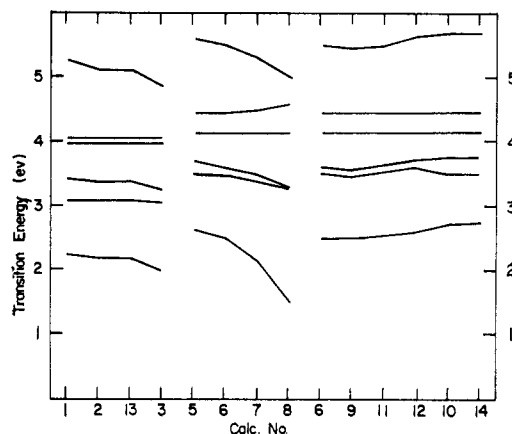


Figure 3. α -Naphthol triplet energy levels.

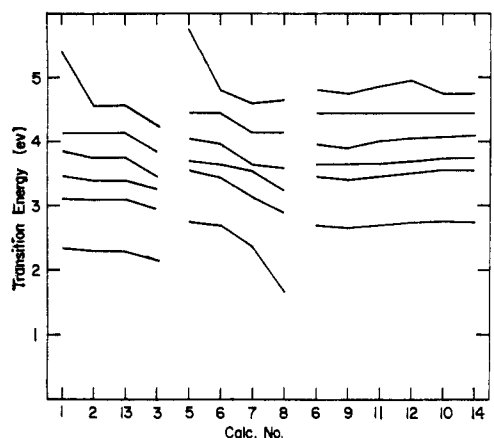


Figure 4. β -Naphthol triplet energy levels.

agreement with experiment.²² The "best" value is 33 e.v., very close to that obtained from Paolini's formula,¹⁶ 32.89 e.v., and 33.182 e.v.¹⁴ This parameter was set at 33 e.v. for the remainder of the calculations.

(2) The variations of β_{CO} (-1.70 to -2.40 e.v.) and γ_{OO} (16.860 to 21.532 e.v.) have little effect on the singlet transition energies (*cf.* calculations 6, 9, 11, 12, and 14).

The results of similar calculations on aniline are equally satisfactory when viewed in this rather non-restrictive manner.²³

A more demanding criterion for the success of the method is quantitative agreement between the calculated and observed changes in the naphthalene transition energies produced by hydroxyl substitution. The spectra were obtained in isoctane solution. It is found (*vide infra*) that the π -electron dipole moments in the 1L_a and 1L_b states are larger than the ground-state moments and hence the net dipole moments in the ground and excited states differ in magnitude. This factor would tend to shift the naphthol transitions to higher or lower energies depending on the sign of the difference between the ground- and excited-state net moments.²⁴

The observed shifts should be corrected for this effect before comparison with the calculated shifts. This uncertainty precludes a strict test of the calculations by this shift criterion, but on the basis of the

(22) H. Baba and S. Suzuki, *Bull. Chem. Soc. Japan*, **34**, 82 (1961).

(23) J. E. Bloor, P. N. Daykin, and P. Boltwood, *Can. J. Chem.*, **42**, 121 (1964).

(24) N. S. Bayliss and E. G. McRae, *J. Phys. Chem.*, **58**, 1002 (1954).

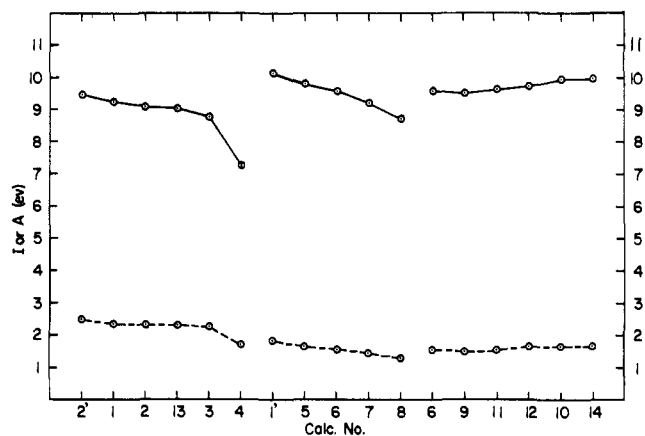


Figure 5. Ionization potentials, $-\epsilon_1$ (solid lines), and electron affinities, $-\epsilon_1'$ (broken lines), for α -naphthol. The corresponding ionization potentials for β -naphthol are 0.1–0.2 e.v. larger and the electron affinities are 0.03–0.1 e.v. larger.

1L_a and 1L_b shifts, the “best” parameters are $W_O = 33$ e.v., $\beta_{CO} = -2.115$ e.v., and $\gamma_{OO} = 21.532$ e.v. Either set of γ_{pq} may be used.

Triplet States. The triplet state energies (Figures 3 and 4) are more sensitive to W_O than the corresponding singlet state energies. With all parameter combinations, the 3L_a energy is somewhat smaller for α -naphthol than for β -naphthol. The calculations indicate a reduction in the 3L_a energy by hydroxyl substitution.

Ionization Potentials and Electron Affinities. The ionization potentials and electron affinities are approximately given by the orbital energies associated with the highest occupied and the lowest vacant orbitals, $-\epsilon_1$ and $-\epsilon_1'$, respectively.¹⁸ These quantities are shown in Figure 5. The ionization potential of naphthalene is 8.26 e.v.²⁵ and although the experimental electron affinity is unknown, it is very small (or negative).²⁶ The quantities are not known for the naphthols, but the ionization potential of phenol is about 0.75 e.v. less than that of benzene,²⁷ a situation roughly in accord with the calculated differences in the naphthalene and naphthol values. We may estimate the naphthol ionization potentials by adding the appropriate differences in the naphthol and naphthalene SCF orbital energies to the observed ionization potential of naphthalene; that is, $I_{est} = \epsilon_1(\text{naphthalene}) - \epsilon_1(\text{naphthol}) + 8.26$ e.v. This leads to the following values (calculation numbers in parentheses): α -naphthol, 7.85 (2) and 7.67 e.v. (6); β -naphthol, 7.99 (2) and 7.85 e.v. (6).

Ground-State and Lowest-Excited-State π -Electron Distributions. The next higher level for testing the adequacy of the SCF formalism involves the calculation of charge distributions. The ground-state π -electron distribution is reflected in the ground-state dipole moment (μ_π). These are quite sensitive to the parameter choice (Figure 6). Since the magnitude of μ_π is unknown, these results cannot be used to choose the best parameters. It is, however, significant that all of the calculations predict that μ_π of β -naphthol is

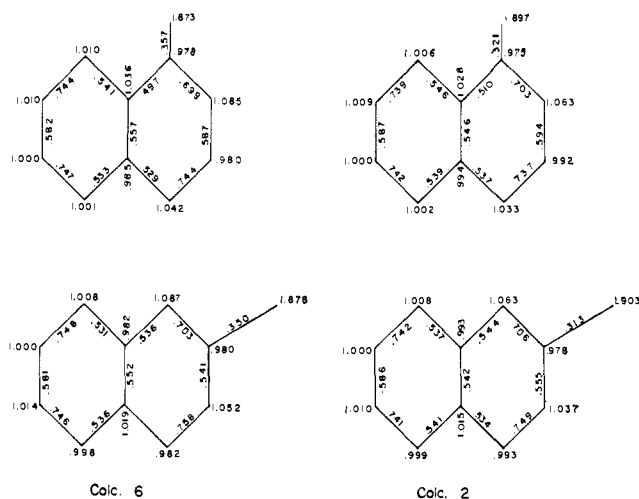


Figure 6. Molecular diagrams: π -electron densities and bond orders.

somewhat larger (5–10%) than the α -naphthol value. The Hückel method leads to the opposite result.

Similarly, although the charge densities are dependent on the parameters, the order of the charge densities is $q_2 > q_4 > q_3$ for α -naphthol and $q_1 > q_3 > q_4$ for β -naphthol. Hence, any correlation (or lack thereof) of π -electron densities and substitution patterns in electrophilic reactions is not dependent on the parameters used.

Upon excitation, the π -electron distribution is altered. In the 1L_b state the results of calculation 2 are ($q_1 - q_{11}$, respectively) α -naphthol: 0.939, 1.037, 1.020, 0.958, 0.999, 1.045, 1.035, 1.015, 1.065, 1.039, and 1.848; and β -naphthol: 1.023, 0.974, 1.036, 1.023, 1.026, 1.031, 1.018, 1.015, 1.019, 0.996, and 1.837. This suggests that the acidity and the hydrogen bond forming powers of the naphthols in the excited state should be larger than in the ground state.

Transition Intensities. It has long been apparent that molecular orbital theories are not very useful for the calculation of the intensities of π -electron transitions.²⁸ It is not surprising, therefore, that the calculated intensities are not in accord with experiment.

The 1L_b transitions, although weak, will always be observable because they will not be hidden by more intense bands. This is not true for weak transitions of higher energy. The distinction between observable and hidden bands in Figures 1 and 2 is somewhat arbitrary. The number of “observable” bands predicted by the theory is not unreasonable in light of the experimental spectra,²² but the relative intensities are dependent on the parameters employed.

In general, calculations 2 and 6 yielded roughly the same direction for the transition moments. One striking exception was noted, however. The 1L_b band in α -naphthol is nearly long-axis polarized in calculation 2 but is rotated by about 45° in calculation 6.

Comparison with Other Studies. One feature that distinguishes the present work from previous treatments of α - and β -naphthol^{6,21} is the increased con-

(25) M. E. Wacks and V. H. Dibeler, *J. Chem. Phys.*, **31**, 1557 (1959).

(26) R. S. Becker and W. E. Wentworth, *J. Am. Chem. Soc.*, **85**, 2210 (1963).

(27) K. Watanabe, *J. Chem. Phys.*, **26**, 542 (1957).

(28) C. M. Moser, *J. Chem. Soc.*, 3455 (1954).

Table III. Comparison of SCF and ASMO-CI Results

Ex-cited state	α -Naphthol				β -Naphthol			
	SCF		ASMO-CI ⁶	Obsd. ²²	SCF		ASMO-CI ⁶	Obsd. ²²
Calcn. 6	Calcn. 2	Calcn. 6			Calcn. 2			
A. Transition Energies (e.v.)								
¹ Ψ_1	4.015	3.930	3.928	3.86	3.935	3.854	3.880	3.78
¹ Ψ_2	4.089	4.050	4.010	4.31	4.229	4.232	4.233	4.54
¹ Ψ_3	5.221	5.374	5.246	5.295
¹ Ψ_4	5.383	5.257	5.490	5.40	5.484	5.377
¹ Ψ_5	5.696	5.606	5.707	5.535	5.414	5.53
¹ Ψ_6	5.903	5.637	...	5.80	5.963	5.873	5.896	...
¹ Ψ_7	6.337	6.198	6.169	...	6.115	5.972
³ Ψ_1	2.512	2.213	2.197	...	2.688	2.300	2.273	...
³ Ψ_2	3.480	3.116	3.439	3.088
³ Ψ_3	3.617	3.397	3.388	...	3.663	3.393	3.388	...
³ Ψ_4	4.140	3.983	3.955	...	3.956	3.761	3.792	...
³ Ψ_5	4.453	4.061	4.080	...	4.443	4.145	4.200	...
³ Ψ_6	5.500	5.137	4.810	4.563
B. Transition Intensities (<i>f</i>) and Polarizations								
¹ Ψ_1	0.0391 (-50.0°) ^a	0.0226 (2.7°)	0.013 (X)	0.016	0.0718 (-60.1°)	0.0562 (-62.7°)	0.066 (-64°)	0.0211
¹ Ψ_2	0.237 (78.8°)	0.304 (84.7°)	0.332 (Y)	0.102	0.105 (-75.0°)	0.186 (-74.5°)	0.195 (-76°)	0.0811
¹ Ψ_3	0.0133 (76.4°)	0.0196 (74.1°)	0.155 (1.3°)	0.970 (4.8°)
¹ Ψ_4	0.423 (1.8°)	0.774 (-0.3°)	1.949 (X)	0.328	0.0512 (85.2°)	0.558 (20.5°)
¹ Ψ_5	0.0098 (-68.8°)	0.230 (-13.8°)	1.725 (11.3°)	0.408 (12.8°)	2.037 (10°)	1.06
¹ Ψ_6	1.421 (-2.1°)	0.806 (1.0°)	...	0.892	0.205 (44.3°)	0.191 (-47.3°)	0.763 (-14°)	...
¹ Ψ_7	1.045 (89.3°)	0.895 (89.7°)	0.802 (Y)	...	0.790 (-67.8°)	0.592 (-81.0°)
C. Calculated μ_{π} , D.								
Ψ_0	1.51 (87.5°) ^b	1.36 (86.5°)	1.34 (91°)	...	1.60 (16.5°)	1.40 (17.8°)	1.19 (13°)	...
¹ Ψ_1	3.22 (46.7°)	2.70 (46.3°)	2.71 (21°)	...	4.14 (25.5°)	3.51 (22.4°)	3.75 (21°)	...
¹ Ψ_2	3.87 (39.2°)	3.49 (36.6°)	3.70 (18°)	...	4.13 (26.0°)	3.41 (30.2°)	3.31 (33°)	...

^a Angle between transition moment vector and +*x* axis. ^b Direction of dipole moment relative to +*x* axis.

figuration interaction. In addition to mixing between $\Theta_{1-1'}$, $\Theta_{2-2'}$, $\Theta_{2-1'}$, and $\Theta_{1-2'}$, the configurations represented by $\Theta_{4-1'}$, $\Theta_{3-2'}$, $\Theta_{1-3'}$, $\Theta_{3-1'}$, $\Theta_{1-4'}$, $\Theta_{2-3'}$, and sometimes $\Theta_{4-2'}$, were included. The effect of including these additional configurations is not too large on the transition energies, but the transition intensities and especially the polarization of the ¹L_b band are quite sensitive to the amount of CI (Table III). The conclusion that the α -naphthol Ψ_1 and Ψ_2 resemble closely the corresponding naphthalene wave functions while the β -naphthol wave functions are very different⁶ is still valid, but a small difference in Ψ_1 can result in a markedly different polarization of ¹L_b. The effect is especially pronounced in this weak transition (forbidden in naphthalene) and it is uncertain that calculations of this type will be useful for such polarization predictions.

Conclusions

The results of this study indicate that for calculations of transition energies in compounds with O²⁺ substituents the following parameters are suitable: $W_O = 33.00$ e.v., $\gamma_{OO} = 21.53$ e.v., and $\beta_{CO} = 2.12$ e.v. The two-center repulsion integrals may be computed by either the Nishimoto and Mataga or the Roothaan (with adjusted exponents) formulas. In this latter case, nearest-neighbor integrals must be reduced by about 0.8 e.v.

The appropriate choice of parameters for the calculations of transition intensities and polarizations and charge distributions is still uncertain.

Acknowledgments. We are grateful to the University of Arizona Numerical Analysis Laboratory for providing machine time and to Professor Robert L. Baker for programming assistance.