fragment orbitals are written. Next, nonorthogonal configurations are generated by allocating the valence electrons to the various orbitals in all possible ways. Then, the resulting configurations are grouped into packets, each packet is separately diagonalized to obtain packet substates, the ground state of each packet substate manifold is selected and denoted by Θ_{a0} (where a is the packet index and zero symbolizes the ground state of packet a), or, more conveniently, by Θ_i, where i is a numerical index, and the Θ_i are then diagonalized to produce the final eigenstates. The final ground state is a linear combination of substates, called bond diagrams, each one being a description of one possible, symmetry-allowed way of connecting the two fragments by bonds and/or antibonds. For example, the bond diagrammatic description of the ground state of A=B, where A and B each has two orbitals and two electrons and the upper orbital of A matches the symmetry of the lower orbital of B, and vice versa, is shown below. Θ_1 is a linear combination of 10 configurations generated

by shifting electrons along the dashed lines starting with the parent configuration, Φ_3, and Θ_2 and Θ_3 are each made
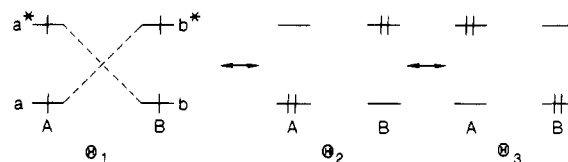
up of one configuration as shown in Figure 4. When the fragment orbitals are capable of strong overlap interaction with each other (i.e., when the AO resonance integrals are large), Θ_1 is the principal bond diagram. Bernardi and Robb and their co-workers have implemented computationally a version of this approach in their independent work.[26]

(26) Bernardi, F.; Olivucci, M.; Robb, M. A.; Tonachini, G. *J. Am. Chem. Soc.* 1986, *108*, 1408 and previous papers.

Properties of Organic Diradicaloid Molecules Predicted by Semiempirical Molecular Orbital Theory. A Practical Procedure

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Semiempirical INDO and MNDO molecular orbital methods yield good results for both geometries and triplet–singlet (T–S) state ordering for a number of diradicals that have recently been examined experimentally. The putative pentamethylenepropane class of diradicals is computed to favor a triplet ground state, even though its members are formally disjoint. Diradicals 7–10 and bicyclic molecules 15–17, formally related to tetramethyleneethane by heteroatom bridging, show a range of electronic nature from strongly diradicaloid for 3,4-dimethylenecyclopentadiene (7) to closed-shell zwitterionic for bicyclic 17. Phenoxy radicals linked by ethylenic units as diradical models (23–25) for oligomeric superparamagnetic polyradicals are found to interact weakly (small T–S gaps), regardless of connectivity.

Introduction

π-Conjugated diradicals are of current interest as reactive intermediates and as tests of quantum theoretical calculations of the properties of an extraordinary form of matter.[1-6] Although ab initio theory is and must remain the method of choice for rigorous computational prediction of electronic properties of diradicals, it places constraints on the size of the molecules for which practical calculations can be done with presently available resources. Hence, semiempirical methods remain useful for qualitative and semiquantitative evaluation of trends among structurally analogous, moderately large molecules, including diradicals and related species.[7]

In this paper we apply semiempirical molecular orbital plus configuration interaction (MO–CI) methods in the study of the ground-state multiplicities and molecular structures of several diradicals under current investigation. We also explore two new kinds of species, one derived hypothetically by heteroatom substitution for the 3- and 7-CH units of pentalene, and the other belonging to the

non-Kekulé series of stilbene dioxys. We find our results in good accord with other theoretical and experimental work (where available) for both molecular geometries and spin-state ordering, and we show the usefulness of the algorithm for examination of systems likely to be of particular interest to experimental chemists in the near future.

(1) See for example (a) *Diradicals*; Borden, W. T., Ed.; Wiley: New York, 1982. (b) Michl, J., Ed. *Tetrahedron, Symposia in Print* 1982, *38*, 733. (c) Berson, J. A. In *The Chemistry of Functional Groups—Quinones*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1988 Vol. 2; chapter 10.
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(3) (a) Du, P.; Hrovat, D. A.; Borden, W. T.; Lahti, P. M.; Rossi, A. R.; Berson, J. A. *J. Am. Chem. Soc.* 1986, *108*, 5072. (b) Du, P.; Borden, W. T. *J. Am. Chem. Soc.* 1987, *109*, 930.
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(6) (a) Dowd, P.; Chang, W.; Paik, Y. H. *J. Am. chem. Soc.* 1986, *108*, 7416. (b) *Ibid.* 1987, *109*, 5284.
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Computational Methods

All computations were carried out on a Celerity C-1260-D computer with use of the MOPAC[8] and ZINDO[9] programs as slightly modified to run on this system. In finding the relative energies of states of different multiplicity for polyradicals, we used Zerner's INDO method as fully described elsewhere.[10] Zerner's method is particularly suited to computation of electronic spectral states, but is not as clearly parameterized as MOPAC for generalized geometry optimization. All molecular state energies were found by self-consistent field MO-CI semiempirically parameterized methods at fixed geometries (SCF–MO–CI using limited single and double excitations selected by methods described previously[9,10]), which we shall herein refer to as INDO–CISD computations. The maximum CI matrix in our computations contains 210 configurations, hence constituting a modest CI method.

A drawback of a previous algorithm[7] for prediction of state multiplicities of diradicals was the use of assumed (typically regular polygonal) molecular geometries. This drawback becomes insupportable when, as in a number of cases we have studied, the use of an assumed geometry leads to nonconvergent results in the SCF–MO portion of the computation. In order to introduce effects of geometry into the model but still retain computational parsimony, we optimized all the geometries with the MOPAC program (MNDO[11] hamiltonian) by using triplet unrestricted Hartree–Fock (UHF) wave functions.[12a] We consider the MNDO–UHF triplet geometries as reasonably good approximations to ab initio geoemetries, rather than quantitatively "correct" structures for the given species under any particular set of conditions. Our treatment of the states of various multiplicity simplistically assumes the triplet UHF geometry as fixed for all states. A completely consistent treatment might optimize states of different multiplicity separately. At the ab initio level, where one aims at maximum precision in a single case, this procedure is needed, but since we aim mostly at trends in energy splittings between spin states of compounds, the present treatment probably is sufficient.[12b]

For the same reasons, the effects of spin contamination upon the UHF-optimized geometries should not be large enough to affect our qualitative findings. Contamination of the ground-state wave functions of molecules by contributions from states of higher multiplicity is a well-known artefact of the UHF method.[13] While some effect of such contamination is expected, the influence on geometries will probably be small at our level of computation. Actually, it has been shown[2a,3a] that the use of UHF wave functions partially recovers the correlation energy in optimizations of diradical geometries, a benefit that should offset contamination effects. We find that even the use of CI in the MNDO optimizations for multiplet states makes only small differences in geometry for small diradical test cases. Given the small geometric changes likely to be caused by
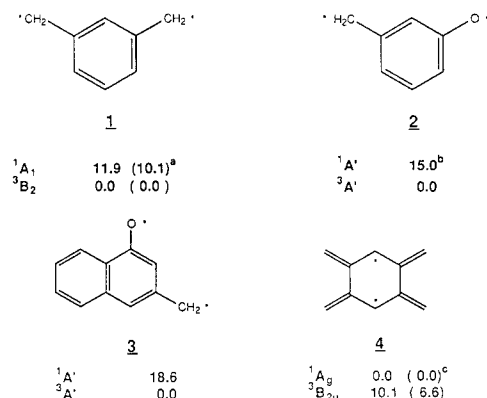
(8) Stewart, J. J. P. *QCPE Program Exchange*, Program 455, **1983**.

(9) Zerner, M. C.; Ridley, J. E.; Bacon, A. D.; Kirchner, R. F.; Cameron, A. Program ZINDO, Florida Quantum Theory Project, Gainesville, FL.

(10) (a) Zerner, M. C.; Ridley, J. E. *Theor. Chim. Acta* **1973**, *32*, 11. (b) Zerner, M. C.; Ridley, J. E. *Theor. Chim. Acta* **1976**, *42*, 233.

(11) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899 and 4907.

(12) (a) Spin-unrestricted (UHF) wave functions tend to give better, more delocalized geometries for conjugated open-shell systems—due to partial inclusion of electron correlation effects—than do spin-restricted (RHF) wave functions. Cf. ref 2a. (b) Clearly, this procedure is not recommended for making predictions of trends in actual molecular geometries of a series of compounds of differing ground-state multiplicity.

(13) Pople, J. A.; Beveridge, D. A. *Approximate Molecular Orbital Theory*; McGraw-Hill: New York, 1970; p 53.

Figure 1. INDO–CISD relative state energies for benzenoid diradicals. All relative energies (kcal/mol) using INDO/CISD at triplet MNDO–UHF geometries. All numbers in parentheses are ab initio numbers for comparison to the INDO/CISD relatives. [a]Reference 2a. [b]π,π^* $^1A'$ state. [c]Reference 3a.

using more elaborate geometry optimization procedures, a worthwhile increase of confidence in results would probably not be realized at a semiempirical level of theory.[12b]

Results and Discussion

Comparison of triplet MNDO–UHF geometries with ab initio geometries is generally satisfactory (see supplementary material for MNDO–UHF geometries). Computed C–O bond lengths of ~125 pm are found in oxaradical cases; by comparison to studies on oxyallyl[14] and related systems at split-valence basis set levels, these values appear 5–10 pm too short. We did not correct for these discrepancies in MNDO predictions versus ab initio expectations, since small geometric variations (save those that break symmetry) would have minor effects on the overall precision of our method as discussed above. Relative INDO–CISD energies for the states of these systems are listed in the various figures, with literature ab initio comparisons where possible. The comparisons demonstrate the efficacy of using the MOPAC geometries for finding state energies by INDO–CISD. We refer the reader to the supplementary material for detailed diagrams of bond lengths and angles. Salient geometric features are mentioned in the text for cases of interest, classified by group below.

***m*-Quinonoid Diradicals.** *m*-Benzoquinodimethane (1) has been treated at a relatively high level of SCF–MO–CI ab initio theory,[2a] by which it has a $^3B_2$ ground state about 10 kcal/mol below the lowest planar $^1A_1$ state, in qualitative agreement with experimental ESR results.[2b-d] *m*-Benzoquinomethane and *m*-naphthoquinomethane (2–3) are likewise found experimentally to have triplet ground states.[2e] Use of our algorithm for 1–3 correctly yields the experimentally observed ground-state multiplicities (Figure 1), with state energy gaps comparable to those obtained in cruder semiempirical calculations.[7]

Notably, the MNDO–UHF geometry of 1 agrees well with the delocalized ab initio $^3B_{2u}$ geometry.[2a] This encourages a level of confidence in the corresponding predictions for 2–3, untested yet by higher level theory, which also show fairly delocalized triplet structures, save for the previously mentioned short C–O• bonds. The computed INDO–CISD T–S gaps are reasonable and comparable for

(14) (a) Osamura, Y.; Borden, W. T.; Morokuma, K. *J. Am. Chem. Soc.* **1984**, *106*, 5112. (b) Lahti, P. M. Ph. D. Thesis, Yale University, New Haven, CT, 1985.
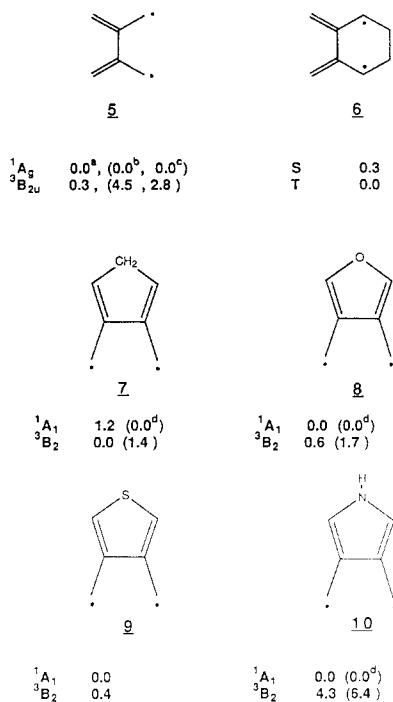
5

¹A$_g$ 0.0[a], (0.0[b], 0.0[c])
³B$_{2u}$ 0.3, (4.5 , 2.8)

6

S   0.3
T   0.0

7

¹A₁   1.2 (0.0[d])
³B₂   0.0 (1.4)

8

¹A₁   0.0 (0.0[d])
³B₂   0.6 (1.7)

9

¹A₁   0.0
³B₂   0.4

10

¹A₁   0.0 (0.0[d])
³B₂   4.3 (6.4)

Figure 2. Monocyclic diradicals derived from tetramethylene-ethane. All relative energies (kcal/mol) using INDO/CISD at triplet MNDO–UHF geometries for π–π* states. All numbers in parentheses are ab initio numbers for comparison to the INDO/CISD relatives. [a]Planar geometry. [b]Planar geometry, Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1977**, *99*, 4587. [c]Nonplanar geometry, ref 3b. [d]Reference 16.

the cases 1–3, bearing in mind that no geometric relaxation for singlet states is used in our model. Geometric relaxation of the singlet states is *not* expected to reverse the large favoring of the triplet state in these cases.

Tetramethylenebenzene. Ab initio theory predicts[3a] TMB 4 to possess a diradical ¹A$_g$ ground state by 6–10 kcal/mol, in violation of the usual interpretation of Hund's rule for molecules. Our semiempirical model concurs, finding a singlet ground state even at an assumed regular polygonal geometry,[7] with a 10 kcal/mol ¹A$_g$–³B$_{2u}$ gap (Figure 1) at the MNDO–UHF geometry. The MNDO geometry is in good agreement with the ab initio geometry,[3a] which shows that TMB is not a cyclically delocalized aromatic molecule (4a) but rather is better described as a union of two pentadienyl radicals joined across inactive sites (4b). Roth has proposed[5] TMB as the carrier of an

4a   **4b**
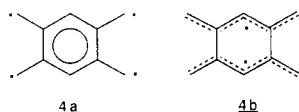
ESR signal generated from a precursor under rigid matrix conditions and has assigned a triplet GS to this molecule. Roth has also interpreted the UV–vis spectrum[5] generated under these conditions as consistent with ab initio predictions for the triplet spectrum.[3a] The cause of the discrepancy between theory and experimental interpretations remains unresolved at present.

Tetramethyleneethanes. We find tetramethylene-ethane itself (TME, 5) to possess nearly degenerate singlet and triplet states, with a slight preference for the singlet at planar geometry (Figure 2). This is in qualitative agreement with the latest ab initio work,[3b] which finds a singlet–triplet (S–T) gap of 2.8 kcal/mol at planar geometries, and an adiabatic S–T gap of 1.7 kcal/mol at non-planar energy-minimized geometries. The related com-

pound 2,3-dimethylenecyclohexa-1,3-diene (6) we actually found to favor a triplet ground state by a slight amount.
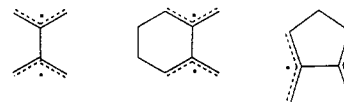
Although the geometries of the π-conjugated portions of 5 and 6 are computed to be similar (disregarding differences in torsion about the central bond), the triplet and singlet states are so closely matched that small geometric changes conceivably could reverse their order at our level of theory.[15] Irradiations of precursors of TME[6a] 5 and its ethano-bridged derivative[6b] 6 have produced triplet ESR signals whose intensities are linear functions of reciprocal absolute temperature (Curie plot). These results permit interpretation either as near-zero S–T gaps or triplet ground states. In both cases[6a,b] the latter interpretation was adopted. The apparent discrepancy between interpretations of experimental and ab initio computational results for ground state multiplicities of TME and related compounds remains unresolved. Hence it is perhaps most prudent simply to note that both our semiempirical and others' ab initio work agree that the gap between singlet and triplet states in these TME's is small.

2,3-Dimethylenecyclopentadiene (DMC) and Heterologues. Compounds 7, 8, and 10 have recently been predicted by Borden et al.[16] to be singlet ground state species related to TME. Comparison of MNDO/UHF–INDO/CISD results to Borden's ab initio results is shown in Figure 2, along with our results for 3,4-dimethylene-thiophene, 9. In agreement with the ab initio work, we find 3,4-dimethylenepyrrole (10) to have the largest singlet-triplet (S–T) gap of the series. The MNDO–UHF geometries agree with the ab initio finding that these DMC derivatives are weakly perturbed TME's (see below).

INDO–CISD finds a triplet ground state for 2,3-dimethylenecyclopentadiene, 7, just as for the higher homologue 6 (see above), formally contradicting the ab initio result.[16] Roth has recently presented experimental UV–vis and ESR evidence in favor of a triplet ground state for the 5,5-dimethyl derivative of 7.[17] The MNDO–UHF geometries for planar TME and for bridged analogues 6 and 7 all have long (>150 pm) transannular bonds between allyl portions of these systems. Thus, geometric perturbation by methylene bridging in TME to give 7 is minor at our level. As with 6, the discrepancy between experimental and ab initio theoretical interpretations of the ground state multiplicity of 7 is unresolved at present, but we again note that ab initio theory and our treatment agree that the T–S gap in 7 should be quite small, whatever the actual ground state under a particular set of conditions.

The similarity of results computed for 3,4-dimethylenefuran and 3,4-dimethylenethiophene (8 and 9) is remarkable. Both are singlet ground states with non-delocalized geometries, by our method and by ab initio

(15) We also find that the triplet state of TME 5 itself decreases in energy relative to the singlet upon torsion about the central bond, with a T–S gap of 3 kcal/mol at the MNDO–UHF triplet bisected geometry. The actual order of states is questionable in this calculation, since the INDO–CISD method depends to some extent upon σ–π orbital separability,[10] and since the CI of our method is too small to deal with a system the does not have clear σ–π separability. Du and Borden[3b] find TME to be a singlet at all geometries where appropriate geometry relaxation is allowed, although the triplet becomes more favorable relative to the singlet at twisted geometries.

(16) Du, P.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1986**, *108*, 8086.

(17) Roth, W. R.; Kowalczik, U.; Maier, G.; Reisenauer, H. P.; Sustmann, R.; Mueller, W. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1285.
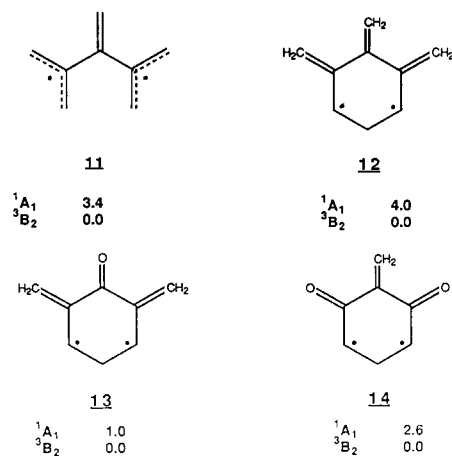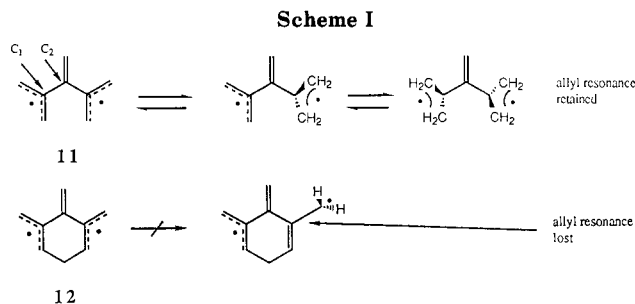
Scheme I

Figure 3. Pentamethylenepropane derived diradicals. All relative energies (kcal/mol) using INDO/CISD at triplet MNDO–UHF geometries.

methods.[16] Experimental results spurred by preliminary semiempirical findings[7] appear to confirm these predictions by spectroscopic (UV–vis, ESR, NMR) and trapping studies.[18-19] Molecules 7–10 may all be classified as quasi-disjoint, since they are through bridging related to TME, but as nonalternant π-systems (save for 7) are not strictly speaking amenable to a simple parity-based formulation[20,23] of disjointness. In retrospect, the similarity of computed S–T gap magnitudes and geometries for 4–10 show that bridging atoms are not large perturbations, although they can still be important in deciding the actual ground-state multiplicity in the finely balanced TME system. Thus, experimental results for 7–10 support the ground state multiplicity predictions of INDO–CISD, while the MNDO–UHF optimizations give geometric information (calibrated relative to ab initio theory[16]) useful for understanding the structural nature of these species.

Pentamethylenepropanes. In their early paper describing the disjoint class of diradicals,[21] Borden and Davidson described the pentamethylenepropane (PMP) diradical species as disjoint[21] and predicted a favoring of the singlet state relative to the triplet in this system.[22] Results for the parent system 11, when constrained to planarity, are shown in Figure 3. The MNDO–UHF (supplementary material) structure shows substantial localization of the two radical centers, with C–C bond lengths of 148.6 pm joining the inactive central sites of the two outlying allyl fragments to the 1,1-ethene moiety. Despite this localization, which should favor the singlet state, INDO–CISD predicts a triplet ground state by 3.4 kcal/mol at the MNDO–UHF triplet geometry.

PMP 11 might well be expected to undergo torsion about the 1,1-ethene bonds connecting the two π-allyl units to the central ethene moiety. Torsion about the 1,1-ethene positions would still leave the dominant allyl resonances of the PMP π-system intact, with loss only of the minor ethene–allyl cross-conjugation across the long C_1–C_2 bond

(see Scheme I). By comparison, a constrained PMP such as 12 and isoelectronic derivatives would not be expected to undergo torsion about the analogous ethene–allyl connections for steric reasons, and would as well be expected not to undergo exocyclic methylene torsion, due to loss of the dominant allyl resonance in the π-system.

The potential nonplanarity of parent PMP 11 would make it a poor experimental test of the disjointness criterion. Methylene-bridged derivative 12 would be far better due to its constrained geometry, assuming that exocyclic methylene torsion is indeed unfavorable. Despite a fairly localized MNDO/UHF geometry, 12 is a ground state triplet by 4 kcal/mol at the INDO–CISD level. The modest T–S gap for both 11 and 12 is in agreement with a less rigorous interpretation of the disjointness criterion, which implies that in such systems singlet states are less unfavorable relative to triplet states than in nondisjoint systems. The prediction of a triplet ground state is in agreement with both the Longuet–Higgins NBMO model of diradicals[20] and the Ovchinnikov valence-bond model.[23] In addition, recent ab initio work[24] predicts a triplet ground state for 12.

In addition to bridged derivative 12, derivatives 13 and 14 were also found to be ground-state triplets by INDO–CISD, but by smaller margins. Still, the effects of heteroatom substitution here are fairly small. Systems 12–14 are all of the same ilk, with modest T–S gaps due to disjointness, but with triplet states favored. The overall INDO–CISD results are of great interest, since it appears that PMP is a finely balanced diradical where small effects could favor either a triplet or singlet ground state. One of us is at present attempting the experimental generation of PMP derivatives, so experimental scrutiny of these predictions may soon be possible.

Diheteroatom-Bridged TME's. Noting the apparently minor effects of TME bridging upon computed S–T gaps for the monocyclic species 7–10, we investigated the effect of double bridging of TME to yield 15–17. INDO–CISD results for S–T gaps are summarized in Figure 4.

The nature of thienothiophene 16 has been explored in earlier theoretical papers at the PPP–SCF,[25a] CNDO/2,[25b] and CNDO/S–CI[25c] levels.[25d] The first two calculations gave conflicting results, but the CI calculation[25c] predicted a singlet ground state 31.8 kcal/mol below the lowest triplet. The aromatic character of the $(4n + 2)$ π-electron system of 16 was apparent from the computed conjugative stabilization energies, 94 and 138 kcal/mol at the sp and spd levels, respectively.[25c]

(18) Stone, K. J.; Greenberg, M. M.; Goodman, J. L.; Peters, K. S.; Berson, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 8088.

(19) Zilm, K. W.; Merrill, R. A.; Greenberg, M. M.; Berson, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 1567.

(20) (a) Longuet-Higgins, H. C. *J. Chem. Phys.* **1950**, *18*, 265. (b) Longuet-Higgins, H. C. *Theor. Org. Chem., Kekulé Symposium*; Butterworth: London, 1958; pp 9–19.

(21) Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1977**, *99*, 4587.

(22) Cf. the excellent description of special connectivity effects on diradical state energy ordering set forth in ref 1a.

(23) (a) Ovchinnikov, A. A. *Theor. Chim. Acta* **1978**, *47*, 297. (b) Misurkin, I. A.; Ovchinnikov, A. A. *Russ. Chem. Rev. (Engl.)* **1977**, *46*, 967.

(24) (a) Borden, W. T., private communication. We thank Prof. Borden for permission to refer to this work in advance of publication. (b) Lahti, P. M., unpublished data.

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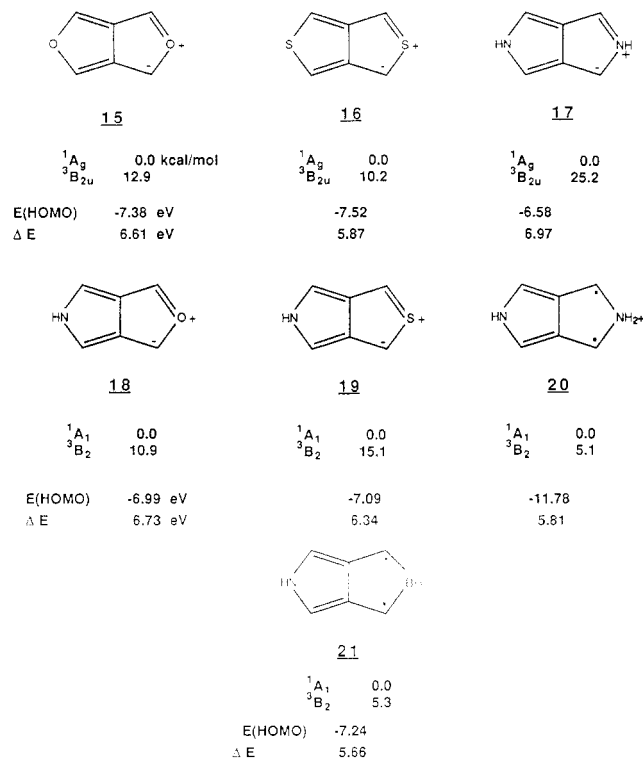
$$^1A_g \quad 0.0 \text{ kcal/mol}$$
$$^3B_{2u} \quad 12.9$$

E(HOMO) -7.38 eV
ΔE 6.61 eV

$$^1A_g \quad 0.0$$
$$^3B_{2u} \quad 10.2$$

-7.52
5.87

$$^1A_g \quad 0.0$$
$$^3B_{2u} \quad 25.2$$

-6.58
6.97

$$^1A_1 \quad 0.0$$
$$^3B_2 \quad 10.9$$

E(HOMO) -6.99 eV
ΔE 6.73 eV

$$^1A_1 \quad 0.0$$
$$^3B_2 \quad 15.1$$

-7.09
6.34

$$^1A_1 \quad 0.0$$
$$^3B_2 \quad 5.1$$

-11.78
5.81

$$^1A_1 \quad 0.0$$
$$^3B_2 \quad 5.3$$

E(HOMO) -7.24
ΔE 5.66

Figure 4. Bicyclic heteroatom-bridged tetramethyleneethanes. All relative energies (kcal/mol) using INDO/CISD at triplet MNDO–UHF geometries. E(HOMO) is energy in electron volts of the HOMO at the MNDO level using an RHF singlet wave function at the UHF geometry. ΔE is the HOMO–LUMO gap (eV) at the MNDO/RHF singlet level.

In our work, the properties of the $(4n + 2)$ π-electron systems of the species 15–19 of Figure 4 help to explain an effect that at first seems to be counterintuitive. Imagine the one-electron frontier MO's of the π-systems of 15–19 to be constructed by perturbative interactions of the frontier MO's of TME with those of two heteroatom 2p orbitals in a manner analogous to that proposed[16] for the monocyclic systems 7–10. Superficially, one might have expected that the second heteroatom would be less effective than the first in splitting the HOMO and LUMO energies, because of the usual damping effect of the separation of orbital energies induced by the first perturbation. The one-electron HOMO–LUMO separation strongly influences the actual S–T separation calculated at the CI level because it tends to give more weight to closed-shell configurations. Consequently, one might have expected naively that the S–T gap in the diheteroatom cases 15–19 would be little more than that in the monoheteroatomic cases 7–10. As Figure 4 shows, the calculated INDO–CISD S–T gaps are substantially *larger* for 15–19 when the typically recommended[7,9,10] selected doubles CI scheme is used. That the result is sensitive to the number of π-electrons in the conjugated system is shown by changing the structure to a $4n$ system, as in the ammonium ion 20 or in the borane 21, which both show much reduced S–T gaps by comparison to 15–19.

In our view, the large S–T gaps in 15–19 may be formulated as *a consequence of the completion of the $(4n + 2)$ π-electron system by the second heteroatom.* As is apparent from an inspection of the orbital energies of hydrocarbon π-systems,[25e] the HOMO–LUMO separation in a $(4n + 2)$ ring is about twice as large as in the π-isoelectronic open-chain analogue. We suggest that this special effect of $(4n + 2)$ cyclic conjugation is at the heart of the large S–T gaps in the diheteroatomic systems 15–19.

Table I. Diradical Natures of Some Non-Kekulé Systems As Shown by the Squared-Ratio of the Two Principal Singlet CI Wave Function Coefficients

molecule	(CI coefficient ratio)²	molecule	(CI coefficient ratio)²
"pure diradical"	1.00	15	3.28
7	1.10	16	2.46
8	1.85	17	8.05
9	1.35	18	3.73
10	3.26	19	3.06

Experimental verification of these predictions for the simple parent compounds awaits future work, but results by Cava et al.[26a-d] on tetraphenylthieno[3,4-c]thiophene, 22, and by several workers upon related compounds[26e-g] indicates the existence of substituted analogues. The crystal structure[26h] of 18 is comparable to our MNDO–UHF structure for 15, save for a longer transannular bond in the MNDO structure (151.4 pm) of 15 than is found experimentally for the analogous bond in 22 (145.2 pm).
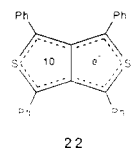
The large preference (10–25 kcal/mol) for a singlet ground state for the diheteroatom bridged species 15–19 relative to the smaller gaps for 7–10 by our procedure leads to the question of when it becomes inappropriate to describe such systems as a diradicals. Qualitatively, the formalism of resonance theory would represent the singlet states in 15–17 as a blend of diradicaloid, zwitterionic, and (for a case such as 16 with third-row elements) hypervalent contributing structures. In SCF–MO–CI terms, one ex-

diradicaloid   zwitterionic   hypervalent
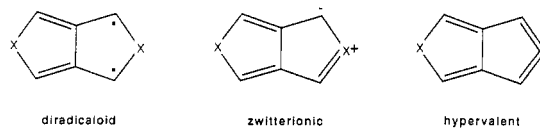
pects increased zwitterionic and hypervalent character to be associated with larger S–T gaps. Zwitterionic states consisting mostly of one or more Kekulé[27a] resonance structures would be notable computationally by a large ratio $(C_1/C_2)^2$ of the squares of the coefficients of the two configurations contributing most to the overall CI wave functions, as pointed out in an earlier analysis of monocyclic molecules 7–8 and 10 by Borden.[16] The large ratio is found because a singlet Kekulé molecule is well described as a *single* dominant $(C_1 \gg C_2)$ electronic configuration with all electrons paired. Alternatively, for a singlet diradical case, $(C_1/C_2)^2$ would be near unity, due to contribution from *two* major configurations shown below yielding

(26) (a) Cava, M. P.; Husbands, G. E. M. J. Am. Chem. Soc. 1969, 91, 3952. (b) Cava, M. P.; Pollack, N. M. J. Am. Chem. Soc. 1967, 89, 3639. (c) Cava, M. P.; Pollack, N. M.; Dieterle, G. A. J. Am. Chem. Soc. 1973, 95, 2558. (d) Cava, M. P.; Behforouz, M.; Husbands, G. E. M.; Srinivasan, M. J. Am. Chem. Soc. 1973, 95, 2561. (e) Sha, C.-K.; Tsou, C.-P.; Wang, S. L. Chem. Commun. 1988, 320. (f) McKeough, D.; Potts, K. T. J. Am. Chem. Soc. 1972, 94, 6215. (g) Potts, K. T. In Heterocyclic Compounds; Weissberger, A., Taylor, E. C., Eds.; Wiley: New York, 1977; Chapter 7, pp 317–379. (h) Glick, M. D.; Cook, R. E. Acta Crystallogr. 1972, B28, 1336. (i) A synthon for benzo[1,2-c:4,5-c]difuran has been reported in Luo, J.; Hart, H. J. Org. Chem. 1988, 53, 1343.

(27) (a) To call "Kekulé" zwitterionic structures such as 15, which has trivalent oxygen and trivalent carbon, could be considered a contradiction in terms. We tolerate this to minimize terminology. See also (b) Greenberg, M. M.; Blackstock, S. C.; Stone, K. J.; Berson, J. A. J. Am. Chem. Soc., in press.

a CI wavefunction of approximately $0.707(C_1-C_2)$. Thus, the squared coefficient ratio in the CI wave function can be taken as a quantitative measure of Kekulé or diradical character. In making such an analysis, we recognize that the absolute values of the computed energies and geometries are sensitive to the type and level of the computation.[27b] Therefore, the results must be interpreted as predictions of qualitative responses of these properties to changes in molecular structure. Our prior experience suggests that useful trends can be discerned despite these caveats. Therefore, we examined the CI wave functions
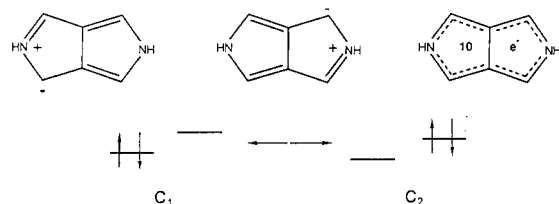

for compounds **7–10** and **15–19** (Table I). Where C_1 and C_2 are the largest two configurations contributing to the function, if $(C_1/C_2)^2$ is not far from unity, the wave function is best described as diradical.[21b] Our results for the monocyclic series **7–10** resemble those of Borden, with both our INDO–CISD and Borden's ab initio wave functions[16] for these species indicating pronounced diradical character. The furan and thiophene derivatives **8–9** are only moderately less diradicaloid (more zwitterionic) than the hydrocarbon **7**. In the monocyclic series, the maximum zwitterionic character is found for pyrrole derivative **10** with $(C_1/C_2)^2 = 3.26$ (ab initio value 2.58[16]), as would be expected from the high electron donor ability for nitrogen. In resonance language, this would correspond to an increased contribution of zwitterionic structures to the resonance hybrid. In fact, the value of $(C_1/C_2)^2$ for monocylic compound **10** is comparable to those for bicyclic compounds **15–16** and **18–19**.

By comparison, di-NH-bridged species **17** has $(C_1/C_2)^2 = 8.05$, showing it to be of essentially zwitterionic, Kekulé nature. Thus, the compounds **7–10** and **15–19** represent a continuum of electronic structure from highly diradical to highly zwitterionic. This continuum shows the imprecision of qualitative definitions of non-Kekulé versus Kekulé molecules. Clearly, both zwitterionic and diradical resonance forms contribute to the electronic natures of monocyclic molecules **8–10**. Only computational results such as the CI wave function give a more quantitive measure of the non-Kekulé or Kekulé nature of a molecule, and then only by comparison to other species. Clearly 2,3-dimethylenecyclopentadiene **7** is a diradical, and di-NH-bridged **17** is a Kekulé molecule. For less clear-cut cases, we may resort to comparison to other molecules.

Borden found that the carbonyl ylid 2-oxa allyl (OA) has $(C_1/C_2)^2 = 5.06$ by an ab initio method, showing the low diradical nature of this species *by comparison* to diradicals **7–8** and **10**, for which he found much lower values.[16] We find the same trend in the INDO–CISD results, the present semiempirical method giving $(C_1/C_2)^2 = 4.3$ for OA, which thus is shown to be more highly zwitterionic than 3,4-dimethylenepyrrole (**10**) and the bicyclic compounds **15–16** and **18**. (However, another semiempirical calculation, AM1–CI[27b] reverses the order of the ratios for **10** and OA).

o-Benzoquinodimethane (OBQ) and *p*-benzoquinodimethane (PBQ), highly reactive molecules that are generally acknowledged to be Kekulé species, have $(C_1/C_2)^2$ by our method equal to 11.5 and 8.8, respectively. Thus, the bicyclic species examined in this section, save for di-NH-bridged **17**, are more diradicaloid that the Kekulé

xylylenes. However, all the mononuclear heterocycles **8-10** are more zwitterionic than singlet *m*-benzoquinodimethane (MBQ) and *m*-benzoquinomethane (MBM), which have $(C_1/C_2)^2$ by our method equal to 1.03 and 1.22, respectively. Both MBQ and MBM singlets are clearly non-Kekulé by this description, despite the fact that singlet MBM might be thought to be well-described by the zwitterionic resonance form shown.
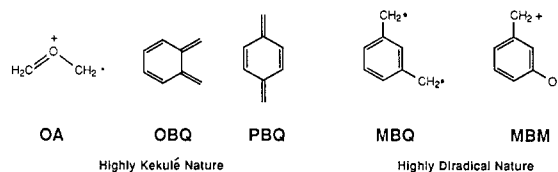
We feel that these computational comparisons help to quantify qualitative expectations concerning which molecules in a homologous series are more zwitterionic than others, as in the comparison of **15–16** to **17**. More important, they allow comparison of the degree of Kekulé character for *different* classes of molecules, a comparison that experimentally is likely to be quite difficult to achieve. By such a comparison, the monocyclic species **7–9** seem to be best described as diradicals, for reasons pointed out by Borden,[16] while diheteroatom bridged **10, 15–16**, and **18–19** occupy an uncertain borderland of electronic nature somewhere between clear distinctions for Kekulé and non-Kekulé molecules. These diheteroatom-bridged TME's are expected to be reactive molecules, with energetically high-lying highest occupied MO's (HOMO's). These expectations appear to be confirmed by the elusiveness of the parent unsubstituted compounds.[26] Compound **17** might be the most likely candidate for a minimally substituted, isolable molecule of this class, due to its very large S–T and HOMO–LUMO gaps. Efforts to synthesize and characterize derivatives of **17** are being carried out by one of us and will be presented in due course.

In summary, until the emergence of experimental methods capable of addressing the question, computational results such as ours may constitute the best evidence[28] that some of the bis-bridged TME class of molecules are better classified as zwitterionic and Kekulé rather than as diradicaloid in the classical sense.

Dioxystilbenes. Much of the interest in diradicals is reflected in the present surge of work upon the synthesis and characterization of potentially ferromagnetic organic materials.[29] As part of our interest in organic superparamagnetic[29c] and high-spin polyradicals, we studied non-Kekulé dioxystilbenes **23–25** as models for interaction of phenoxy radicals through an ethyleneic linkage. By the Ovchinnikov criterion[23] the *o,m'*- and *m,p'*-dioxystilbenes (**23, 25**) are qualitatively predicted as high spin species, while the *m,m'*-dioxystilbene **24** should be low spin. INDO–CISD state energies of these species are shown in Figure 5. Compounds **23** and **24** both show phenyl ring torsion[30] (supplementary material) relative to the plane

(28) Although the computational results reported here are likely to give reliable account of trends of electronic nature as a function of structure, their reliability in any specific case in predicting the actual blend of diradicaloid and zwitterionic character or the actual magnitude of a given T–S gap remains untested experimentally at present. The only independent checks of the INDO–CISD results on wave function makeup and T–S gap magnitude reported here or other semiempirical results given elsewhere[27b] are comparative ab initio calculations, which are also untested. Conceivably, results from both types of computations are systematically displaced relative to reality for specific cases.

(29) (a) Miller, J. S.; Epstein, A. J.; Reiff, W. M. *Chem. Rev.* **1988**, *88*, 201. (b) Miller, J. S.; Epstein, A. J.; Reiff, W. M. *Acc. Chem. Res.* **1988**, *21*, 114. (c) Cf. also footnote 33 in ref 29b.
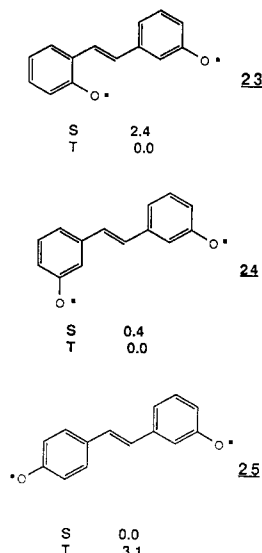
Figure 5. Non-Kekulé dioxystilbenes **23-25**. All relative energies (kcal/mol) using INDO/CISD at triplet MNDO-UHF geometries. Selected bonding parameters show bond lengths in angstroms, bond angles and torsions in degrees.

of the olefin unit. Both are nonetheless ground state triplets at these geometries at the INDO-CISD level; however, the gap is smaller for **24** (0.4 vs 2.5 kcal/mol). INDO/2 spin density analysis[31] of **24** shows the unpaired electron density to be isolated on separate rings with little interaction. To our surprise, despite an essentially planar geometry, the *m,p'*-isomer **25** was found to be an open-shell ground-state singlet by about 3 kcal/mol by using a variety of orbital selection patterns in carrying out CI. Spin density analysis of the $\pi-\pi^*$ triplet state of **25** showed the expected alternate distribution of spin with no anomalies.
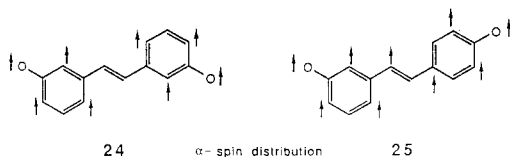
The results for **23** and **24** are in good accord with previous qualitative predictions. Essentially, **24** behaves as a pair of well-separated radicals, yielding little significant interaction or triplet-singlet splitting, while **23** retains sufficient interaction between unpaired electrons to yield discrete triplet and singlet states. The difference is qualitatively attributable to localizability of the SOMO's of the *m,m'*-isomer **24** to be on noncommon π-centers, leading to lack of interaction (disjointness, Ovchinnikov N* = N₀) in the unpaired electrons. The nondisjoint nature of the *o,m'*-isomer conversely leads to a favoring of the triplet state.

By the same argument, one expects the *m,p'*-isomer **25** also to favor a triplet ground state. The reason for the observed $\pi-\pi^*$ singlet ground state is unclear in our model.[32] The CI wave function of the singlet is a mixture

of open-shell singlet configurations, with the major configuration being single occupation in the two highest occupied MO's. Even more confusing is the fact that the corresponding diradical to **25** where each oxygen is replaced by a methylene group is found to have the expected triplet ground state by 4.2 kcal/mol at the MNDO-UHF geometry. If the INDO-CISD results are anywhere near reality for **25**, then oxy substitution upon this alternant system is exerting more influence on the ground-state multiplicity than we have computed in other, similar systems. Overall, it appears that in dioxystilbenes ground-state multiplicity choice is finely balanced with small T-S gaps, representing a potentially more complex problem in spin coupling than simple qualitative models might initially lead one to believe.[20,23] One of us is at present carrying out experiments in an effort to check the computational predictions for **23-25** and will report on the results of this work in due course.

Conclusions

We find the combination of MNDO-UHF and INDO-CISD computations to be effective in giving both geometries and relative energies for spin states of diradical and diradicaloid systems. MNDO geometries, although somewhat more localized than model ab initio geometries, are quite acceptable in finding experimentally verifiable state-energy ordering by semiempirical MO-CI methods and in judging the qualitative nature of interactions in a given molecule. Specific conclusions by this procedure are as follows:

(1) The *m*-quinonoid diradicals are qualitatively well-described. All possess triplet ground states, regardless of heteroatom substitution or extended benzannelation, in qualitative agreement with experiment. Computational T-S gaps are predicted to be large for all members of this family.

(2) The strictly disjoint diradicals related to TME (**4-7**) have small T-S gaps. Therefore, subtle effects not clearly identified could play a major role in determining the actual ground-state multiplicity. An exception is TMB **4**, for which we concur with ab initio computations in predicting a fairly large preference for the singlet state at all investigated geometries, despite present experimental indications to the contrary.

(3) Analysis of the INDO-CI wave functions agrees with ab initio results in suggesting the predominantly diradical nature of the mononuclear heterocyclic molecules **8-10**. It should be noted that AM1-CI[27b] suggests a steeper rise toward zwitterionic character in this series.

(4) The pentamethylenepropane class of molecules **11-14**, despite their formally disjoint nature, all favor triplet ground states by modest amounts, even with exocyclic heteroatom substitution.

(5) The bicyclic compounds **15-20** display the geometric characteristics expected for weakly perturbed TME's, with long transannular bonds. The CI wave functions prove to be useful in evaluating the relative Kekulé vs non-Kekulé nature for these and other molecules. Analysis of these CI wave functions in a manner similar to that used by Borden[16] for these species shows a range of reduced diradical nature for bicyclic **15-20** relative to monocyclic **8-10**. In the extreme, **17** is best described as a zwitterionic Kekulé molecule. The S-T gaps and HOMO-LUMO gaps of these bicyclic species are also in good accord with a simple $(4n + 2)$ aromatic perimeter model, consistent with their large S-T gaps relative to the monocyclic species.

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(30) However, MNDO is known to favor twisted π-systems in many cases. Cf. a brief discussion of the tendency in Clark, T. *A Handbook of Computational Chemistry*; Wiley-Interscience: New York, 1985; p 150.

(31) Reference 13, p 128 ff.

(32) Further complicating the prediction of ground state multiplicity for **25** is our finding that use of MNDO-CI at the MNDO-UHF triplet geometry—a procedure that gives fairly good agreement with INDO-CISD relative state energies for several of the systems in this study[33]—gives a triplet $\pi-\pi^*$ ground state. While we feel that INDO-CISD is a method better calibrated for prediction of spectroscopic state energies, the difference of MNDO-CI and INDO-CISD results shows a need for experimental conformation of ground state.

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(33) Blackstock, S. C.; Berson, J. A. Unpublished results.

(6) The model dioxystilbenes **23–25** all have modest energetic differences between triplet and singlet states, showing that coupling between radical centers in these molecules is not very strong. We intend to extend our model to larger polyradicals, in order to examine ground-state spin multiplicity as a function of oligomer size.

Overall, the reasonable agreement between our results and ab initio results for several smaller cases shows the usefulness of this method when ab initio computations are not practical.

Registry No. 1, 32714-83-3; 2, 71946-86-6; 3, 76984-35-5; 4, 88017-87-2; 5, 16893-57-5; 6, 118319-53-2; 7, 118319-54-3; 8, 118319-55-4; 9, 118319-56-5; 10, 118319-57-6; 11, 95406-55-6; 12, 118334-59-1; 13, 118319-58-7; 14, 118319-59-8; 15, 118319-60-1; 16, 24976-21-4; 17, 250-30-6; 18, 250-31-7; 19, 35834-36-7; 20, 118319-62-3; 21, 118334-60-4; 23, 118319-63-4; 24, 118319-64-5; 25, 118319-65-6; OA, 61518-27-2; OBQ, 32796-95-5; PBQ, 502-86-3.

Supplementary Material Available: ORTEP-type diagrams for all MNDO–UHF triplet optimized geometries, showing important bond lengths and angles (16 pages). Ordering information is given on any current masthead page.

Polymer-Supported Cation Radicals

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Reaction of chloromethylated polystyrene (3.90 mequiv/g) beads with triphenylamine and diethylchloroalane resulted in a highly cross-linked polymer. The chloromethylated polystyrene was modified by reaction with 2,6-dibromocarbazole (4) and K_2CO_3 in DMF at 100 °C to give an excellent yield of polymer-supported 2,6-dibromocarbazole (5) without concomitant cross-linking. The polymer-bound 2,6-dibromocarbazole was nonreactive toward $SbCl_5$, whereas the homogeneous counterpart 9-*N*-benzyl-2,6-dibromocarbazole (6) was found to readily generate the aminium cation radical upon reaction with $SbCl_5$. Attachment of phenothiazine to a polystyrene support yielded a reagent that would react very rapidly with $SbCl_5$ in dichloromethane. The polymer-bound phenothiazine cation radical was found to readily oxidize the metal–metal bond in $[C_5H_5Fe(CO)_2]_2$ and undergo anion exchange with Bu_4NPF_6 to afford a more synthetically useful reagent.

Introduction

Polymer-bound organic reagents often have one or more advantages over their homogeneous counterparts.[1] One primary advantage to polymer-bound reagents is the facile removal of expended or excess reagent at the completion of the reaction. This can lead to recovery and regeneration of the reagent. We recently demonstrated such a use with polymer-supported 2,6-di-*tert*-butylpyridine, which was shown to be easily recovered and fully regenerated for further reaction.[2]

For over two decades aminium cation radicals have been known to be very efficient one-electron transfer reagents.[3] A more recent use of aminium cation radicals for the mild stoichiometric oxidation of metal–metal bonds in transition-metal complexes[4] prompted us to report our work in the area of polymer-supported cation radicals. Bauld et al. has recently demonstrated that polymer-bound aminium cation radicals were efficient catalysts for certain Diels–Alder reactions;[5,6] however, because of low loading levels of the aminium cation radicals, the utility of the polymer-bound reagents has thus far been limited to catalytic applications.

In this paper we describe our efforts leading to the successful development of polymer-supported cation radical reagents having an equivalent weight that is practical for use as stoichiometric, one-electron oxidants. The polymeric reagent is simply filtered after the oxidation reaction to yield a product that is not contaminated by the expended oxidant or excess reagent.

Results and Discussion

Our initial approach attempted to load triphenylamine onto chloromethylated polystyrene (3.90 mequiv/g) with Lewis acid catalysis. This approach is known to work for chloromethylated polystyrene having 1.09 mequiv of active CH_2Cl per gram of polymer.[5] We find reaction of the more heavily chloromethylated (3.90 mequiv CH_2Cl/gram of polymer, i.e. 50% of the phenyl rings modified) polystyrene with triphenylamine in the presence of diethylchloroalane

(1) For reviews on polymer-supported reagents see: (a) *Polymer*-supported *Reactions in Organic Synthesis*; Hodge, P., Sherrington, D. C., Eds.; Wiley: New York, 1980. (b) Akelah, A.; Sherrington, D. C. *Chem. Rev.* **1981**, *81*, 557. (c) Frechet, J. M. J. *Tetrahedron* **1981**, *37*, 663. (d) Akelah, A. *Synthesis* **1981**, 413. (e) Mathur, N. K.; Narang, C. K.; Williams, R. E. *Polymers as Acids in Organic Chemistry*; Academic Press: New York, 1980. (f) Kraus, M. A.; Patchornik, A. *Macromol. Rev.* **1980**, *15*, 55. (g) Daly, W. H. *Makromol. Chem., Suppl.* **1979**, *2*, 3. (h) Leznoff, C. C. *Acc. Chem. Res.* **1978**, *11*, 327. (i) Heitz, W. *Adv. Polym. Sci.* **1977**, *23*, 1.

(2) Wright, M. E.; Pulley, S. R. *J. Org. Chem.* **1987**, *52*, 5036.

(3) (a) Walter, R. I. *J. Am. Chem. Soc.* **1955**, *77*, 5999. (b) Walter, R. I. *Ibid.* **1966**, *88*, 1923. (c) Bell, F. A.; Ledwith, A.; Sherrington, D. C. *J. Chem. Soc. C.* **1969**, 2719. (d) Hammerich, O.; Parker, V. D. *Adv. Phys. Org. Chem.* **1984**, *20*, 55.

(4) Cummins, C. C.; Kegley, S. E. ACS National Meeting, Denver, CO, 1987; Inorg. Abstr. No. 137.

(5) Bauld, N. L.; Bellville, D. J.; Gardner, S. A.; Migron, Y.; Cogswell, G. *Tetrahedron Lett.* **1982**, *23*, 825.

(6) For examples of radical-catalyzed Diels–Alder reactions, see: Bellville, D. J.; Wirth, D. D.; Bauld, N. L. *J. Am. Chem. Soc.* **1981**, *103*, 718. Gassman, P. G.; Singleton, D. A. *J. Am. Chem. Soc.* **1984**, *106*, 7993.