KEYNOTE
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Paul Dowd and diradicals

Christopher J. Cramer

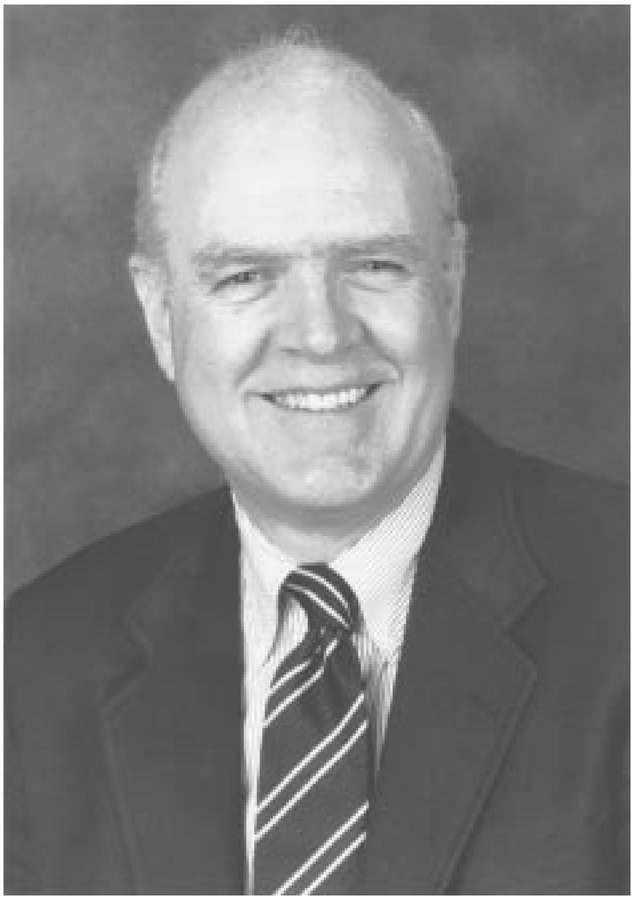
Department of Chemistry, University of Minnesota, 207 Pleasant St. SE, Minneapolis,
MN, 55455, USA

An analysis of Paul Dowd's many contributions to the understanding of organic diradicals is presented.

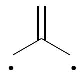
Introduction

This issue of the *Journal of the Chemical Society*, *Perkin Transactions 2* contains a series of papers by researchers active in the study of organic diradicals, and in most instances these are diradicals of the so-called non-Kekulé variety (a non-Kekulé molecule is characterized by having 2*n* pi electrons such that no resonance structures can be drawn with those electrons in *n* double bonds). This focus honors the memory of Professor Paul Dowd (1936–1996), a pioneer in this field whose accomplishments included the experimental discovery and detailed characterization of two of the key paradigmatic non-Kekulé hydrocarbons, namely trimethylenemethane[1,2] (TMM) and tetramethyleneethane[3] (TME).

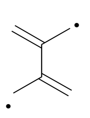
My intent here is to explore some of Paul Dowd's seminal contributions in the area of diradicals. This is *not* structured as a complete historical review of all work in the non-Kekulé area—readers seeking such coverage will be better served by earlier work[4] and/or the individual research articles found elsewhere in this issue. Instead, I hope to provide specifically a sense of the progress of Dowd's efforts in this area, including select biographical information that may be of interest to the reader. Moreover, much of Dowd's detailed experimental work continues to pose certain unresolved questions with respect to the chemistry of TMM and TME, and these points will be highlighted in the penultimate section.



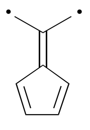
Paul Dowd (1936–1996)



TMM



TME



CpTMM

Years leading to the discoveries of TMM and TME

Paul Dowd received his A.B. degree in Chemistry from Harvard University in 1958. As a student with Professor Ronald Breslow, he pursued graduate study in chemistry at Columbia University, receiving the Ph.D. degree in 1962 for studies directed towards characterization of substituted cyclopropenyl anions. This was a particularly exciting period of time for physical organic chemists—new developments and improvements in kinetic and spectroscopic techniques were opening the door to the study of many new kinds of organic reactions and, in particular, of short-lived or metastable reactive intermediates. Dowd developed a reputation while at Columbia as a chemist with deep mechanistic insights. During weekly departmental meetings dedicated to the solution of novel mechanistic problems, Dowd could always be relied on to have a reasonable proposal for even the most mysterious of reactions.[5] One of his key strengths was an ability to tie together seemingly disparate pieces of experimental data in order to construct a single coherent mechanism. This ability continued to manifest itself throughout his scientific career, including truly remarkable contributions to the understanding of the modes of action of vitamins B_{12},[6,7] E,[8,9] and K,[9,10] that are not further discussed here. Noting this propensity, a colleague, Professor Craig Wilcox, once described him as someone who 'excelled at discovering chemical gems of great practical value.'[11]

In the early 60s, such singular talents inevitably led to postgraduate study with one of a handful of chemists, and in this case it led Dowd to return to Harvard as a postdoctoral associate with the research group of Professor R. B. Woodward. However, Dowd and Woodward's interests failed to overlap as much as either might have hoped. While Woodward was focused on using mechanistic understanding to further the synthesis of complex molecules, Dowd's interest in reactive intermediates tended to be at a more fundamental level—*ars gratia artis*, as it were. Facilitated by his appointment to the Harvard faculty as a lecturer in 1963, Dowd's first publications described independent work focused on the chemistry of highly populated π systems, in particular the dianion of tetraphenylallene[12] and the dianion radical of tetraphenylallyl.[13] While studying the latter, Dowd, with the assistance of Dr A. L. Kwiram, turned to electron spin resonance (ESR) spectroscopy for the characterization of open-shell reactive intermediates. I suspect that

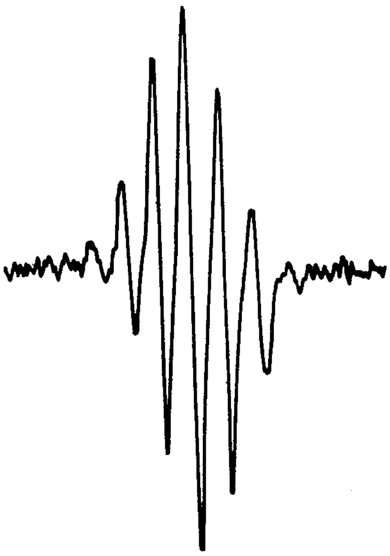
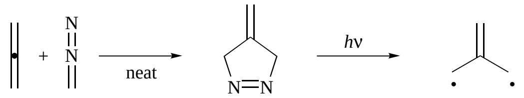


Fig. 1 Single-crystal ESR spectrum of trimethylenemethane. The septet shown, one of two, is the low-field peak. It is centered at 2940 G (klystron frequency 9150 Mc). Much more intense spectra show that *only* seven peaks are present. In the latter case, however, the use of higher power distorts the spectrum enough so that the expected binomial ratio of intensities is not reproduced as well as it is in the spectrum shown above. Reprinted with permission from *J. Am. Chem. Soc.*, 1968, **90**, 2715. Copyright 1968 American Chemical Society.

this event may well have stimulated efforts directed toward the preparation of TMM, since it had been predicted by theory to have a triplet ground state,[14,15] for the detection of which ESR was obviously the ideal choice.

Working entirely on his own, Dowd[1] accomplished the synthesis of TMM in 1966 (Scheme 1). Photolysis of dilute solutions of 4-methylene-Δ^1-pyrazoline † in either hexafluorobenzene or perfluoromethylcyclohexane led to an ESR spectrum (stable for up to one month at 77 K) consistent with a triplet species characterized as having a threefold axis of symmetry and zero-field splitting (zfs) parameters of $D = 0.024$ cm^{-1} and $E < 0.001$ cm^{-1}.[1] These zfs values, in addition to providing information on the structure of the triplet, convincingly settled differences in the theoretical literature over the extent of negative spin density expected for the central carbon of TMM (not the last time Dowd's results would confound select members of the theoretical community!)



Scheme 1

Of some historical interest is the nature of the synthesis used to prepare the photolysis precursor—a one-step procedure not for the faint of heart. The pyrazoline was recovered from a room temperature [3 + 2] cycloaddition of liquid diazomethane with liquid allene (as solvent) in a sealed tube. The product pyrazoline readily isomerizes to the fully conjugated exo-methylene tautomer and is unstable to air, heat, and light. The many attempts undertaken prior to successful completion of the synthesis involved the production of copious amounts of diazomethane—a highly toxic, odorless gas at room temperature and a powerful explosive as a liquid. During this period, Dowd would smoke cigarettes whenever he was working with diazomethane, because there was a prevailing belief that were the gas to be drawn through a burning cigarette, a noticeable change in taste would warn one of its presence![16]

Shortly thereafter, Dowd and Sachdev[17] developed an alternative, simpler synthesis of TMM, using 3-methylenecyclobutanone as the photolysis precursor. This more stable precursor permitted preliminary studies of the chemical reactivity of TMM[18] and also allowed much cleaner ESR spectra to be generated. Indeed, it proved possible to grow a suitable single crystal of this compound (a taxing feat, insofar as the solid melts at −20 °C) and obtain a rotationally resolved spectrum of TMM.[19] When the field strength is aligned along the molecular symmetry axis, TMM shows the binomially symmetric seven-line hyperfine splitting expected for a D_{3h} triplet (Fig. 1).

Dowd's experimental work on TMM stimulated the interest of a then graduate student at Harvard, Weston Thatcher Borden. Prior to beginning his doctoral work with E. J. Corey in 1965, Borden had spent a year studying with the English theoretician H. C. Longuet-Higgins, whose 1950 paper[15] had provided a description of the electronic structure of non-Kekulé hydrocarbons, such as TMM, at the level of Hückel theory. Dowd's experimental work on TMM and conversations with Dowd about TMM led Borden to begin considering the effects of electron repulsion in diradicals. This culminated, some ten years later, in the publication of a general theory of these effects.[20,21]

A crucial element in the development of this theory was an experimental collaboration between Dowd and Borden in 1969, after Borden had joined the faculty at Harvard. They attempted to detect the triplet state of D_{8h} 1,3,5,7-cyclooctatetraene (COT) in a frozen matrix, but the experiment proved unsuccessful. Consideration of possible reasons for this failure led Borden to predict that D_{8h} COT and other diradicals with 'disjoint' non-bonding molecular orbitals violate Hund's rule by having singlet ground states.[22] The experimental verification of a predicted violation of the strictest version of Hund's rule came more than a quarter of a century after Dowd and Borden's unsuccessful, and hence unpublished, experiment. Ironically, the experiment involved formation of D_{8h} triplet COT by photodetachment of an electron from COT radical anion and the observation that formation of D_{8h} singlet COT requires less energy.[23]

Borden credits Dowd's experiments on TMM and COT at Harvard for providing the inspiration for the theory recognizing the differences between disjoint and 'non-disjoint' non-Kekulé hydrocarbons. TMM is the parent non-disjoint non-Kekulé hydrocarbon. The parent disjoint non-Kekulé hydrocarbon, on the other hand, is tetramethyleneethane (TME), which Dowd also became interested in while he was at Harvard.

Dowd's interest in TME was probably enhanced by one of his then colleagues at Harvard, Professor William von Eggers Doering, whose work Dowd always found inspirational.[24] Doering had earlier assigned singlet TME as an intermediate in the degenerate thermal rearrangement of 1,2-dimethylenecyclobutane[25] (a similar inference was made simultaneously by Gajewski[26]). In 1970 Dowd reported the successful generation of TME *via* photolysis of perdeuterio-3,4-dimethyenecyclopentanone,[3] the synthesis of which is illustrated in Scheme 2. In this initial report, the perdeuterio-substrate was required to eliminate line broadening (by ^{1}H hyperfine coupling) of a persistent radical signal in the ESR spectrum and allow the triplet spectrum to be observed ($D = 0.012$ cm^{-1}—no E value could be assigned for this spectrum).

That same year, Dowd left Harvard and moved, together with his wife, Susan, and three children, Katherine, Joseph,[27] and Michael, to Pittsburgh. There he began a position at the University of Pittsburgh, where he would remain for the rest of his career.

The Pittsburgh years

In his first few years at Pittsburgh, Dowd focused his efforts primarily on research directed towards understanding the chemistry of vitamin B_{12}. In 1976, however, he returned to the

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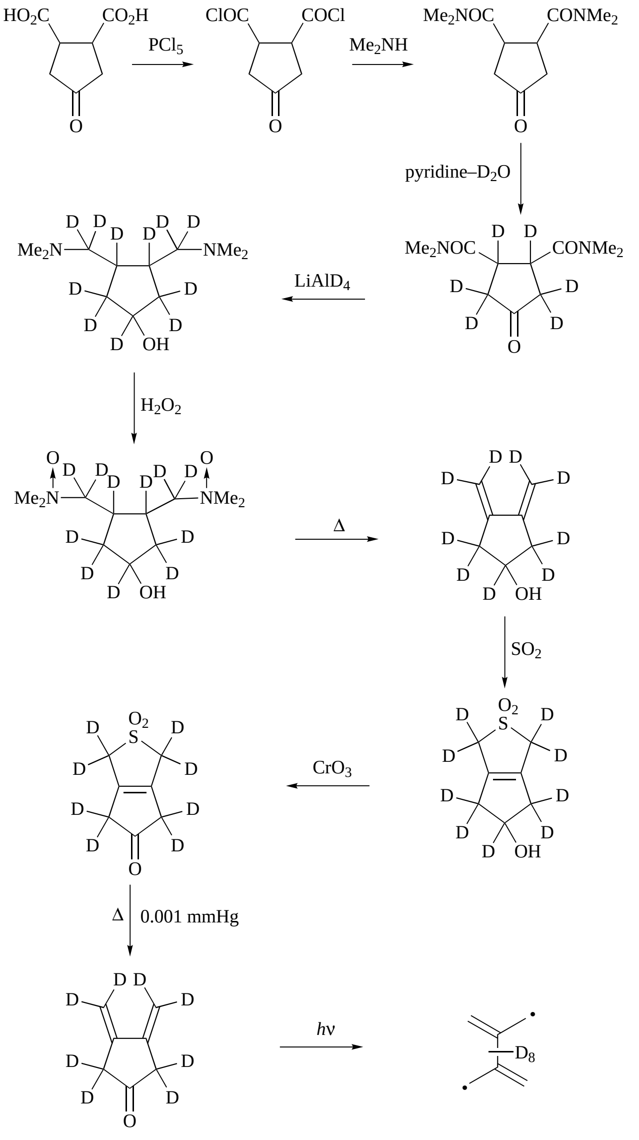
† 4-Methylene-4,5-dihydro-3*H*-pyrazole.



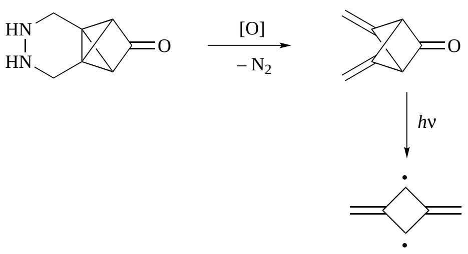
Scheme 2

study of TMM, demonstrating unambiguously that the triplet state was the ground state for this system.[28] Several theoretical studies on TMM had appeared following Dowd's synthesis, and all of them predicted the triplet to be the ground state by a comfortable margin.[29–31] Experimental confirmation was accomplished by the observation of a linear relationship between ESR signal intensity and inverse temperature over the range 20–80 K. Such Curie law behavior sets an upper limit on the singlet–triplet splitting from solution of eqn. (1) where I is

$$I = \frac{1}{T}\kappa(1 + e^{-\Delta/RT}) \qquad (1)$$

the ESR signal intensity, T is the temperature, κ is a constant, Δ is the energy of the lowest singlet state above the triplet, and R is the gas constant. For the temperature range observed, the triplet state must either be the ground state or lie no more than 10 cal mol^{-1} above it (*i.e.*, the triplet ESR signal would arise from thermal population). This observation of Curie law behavior for TMM coincided with another experimental study by Platz *et al.*[32] demonstrating several substituted TMMs to have triplet ground states. Very recently Wenthold *et al.*[33] reported the photoelectron spectrum (PES) of the TMM radical anion; the gas-phase S–T splitting for TMM was found to be 16.1 kcal mol^{-1}.

In 1986 (Dowd's work in the diradicals area between 1976 and 1986 is discussed primarily in the next section) Dowd and Paik[34] reported the synthesis of dimethylenecyclobutadiene from the photolysis of dimethylenebicyclo[1.1.1]pentanone (Scheme 3). Dowd somewhat whimsically referred to this diradical as 'an edge-to-edge double trimethylenemethane,'[34] perhaps because, like TMM, this benzene isomer had also been predicted[35,36] to have a triplet ground state. Irradiation of the ketone in the presence of acetophenone as a triplet sensitizer generated an ESR spectrum identical with that reported a few months earlier by Snyder and Dougherty[37,38] (these latter workers had employed an analogous azo precursor).



Scheme 3

Interestingly, in the absence of acetophenone as a sensitizer, Dowd and Paik[34] reported the generation of a different triplet spectrum. By analogy to spectral features relating *m*-xylylene[39] and *m*-quinomethane,[40] this spectrum was assigned to 3-methylenecyclobutanone diradical. This observation was of particular interest because Curie plots for both diradicals indicated them to be ground state triplets, while the diradical from cyclobutane-1,3-dione had been predicted to be a ground singlet by a comfortable margin.[41,42] This work thus represented one of the first contributions towards our understanding of how heteroatomic substitution affects relative state energies in non-Kekulé systems, a subject that continues to be of interest and indeed is the primary topic of two papers contributed to this issue.[43,44]

The embedding of TMM and TME into various ring systems was always of particular interest to Dowd. In 1991, he showed that simple Hückel theory predicted fivefold and sixfold orbital degeneracies for tris(cyclopentadienyl)trimethylenemethane and tetrakis(cyclopentadienyl)tetramethyleneethane, respectively.[45] Such high degeneracy is, of course, an artifact of the quantitative inaccuracies inherent in Hückel theory, but the qualitative implications for the possibility of multiple low-energy states, many of high spin, remain intriguing. In order to follow this work up more thoroughly, Dowd carried out a much higher level theoretical investigation[46] of cyclopentadienyltrimethylenemethane (CpTMM) in collaboration with his Pittsburgh colleague, Professor Ken Jordan (the first collaboration between these two is described in the next section). This work predicted a triplet ground state for CpTMM, with the first singlet lying 4.9 kcal mol^{-1} above the triplet.

While Dowd was appreciative of the contributions that could be made by electronic structure theory, he was an experimentalist through and through! When Professor Joseph Grabowski, a gas-phase ion chemist, joined Pittsburgh's faculty, Dowd began working with him to generate the radical anion of CpTMM in the gas phase in order to check the theoretical predictions. Photoionization of said radical anion would allow assignment of the ground state (typically making use of theory to assign states based on vibrational band structure) and direct measurement of the S–T splitting (as accomplished by Wenthold *et al.*[33] for TMM). In 1996, Zhao, Dowd, and Grabowski reported the successful generation of CpTMM radical anion in the gas phase from reaction of the corresponding fulvene with $O^{\bullet-}$.[47] This procedure was also demonstrated to be effective for other related fulvenes, suggesting that it may prove quite useful for the systematic examination of substitution effects on diradical multiplet splitting in these systems, assuming the photoelectron spectra prove interpretable. Similar efforts to generate the radical anion of TME in the gas phase were also described by Grabowski and Dowd,[48] and the

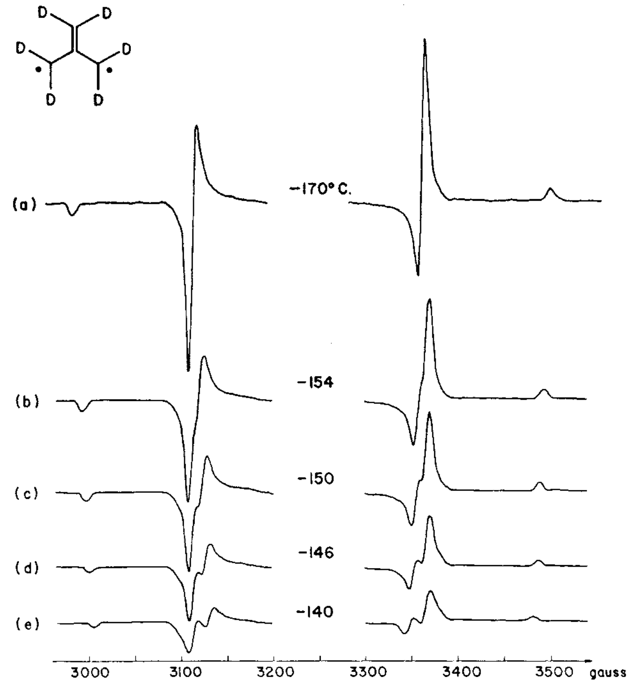


Fig. 2 Electron spin resonance spectrum of [$^2H_6$]trimethylenemethane, from γ-radiolysis of neat [$^2H_6$]methylenecyclopropane, showing the change in the *xy* and *z* lines as a function of temperature. Reprinted with permission from *J. Am. Chem. Soc.*, 1977, **99**, 2825. Copyright 1977 American Chemical Society.

measurement of its photoelectron spectrum is discussed further in the next section.

The work of Zhao *et al.*[47] appeared only a month before Dowd's death. Though battling cancer, Dowd's attraction to chemistry (and his ability to take comfort from it) was so strong that he continued to spend time in his departmental office with his research group until three days before the end.

Always working at the frontiers, Dowd's work challenged conventional wisdom and oftentimes taxed the limits of available theoretical methods. The next section is devoted to the discussion of different results from Dowd's laboratories that continue to raise questions about certain features of the chemistries of TMM and TME.

Unsolved mysteries

Loss of symmetry in triplet TMM. Immediately following his arrival at Pittsburgh, Dowd generated the triplet ESR signal of TMM by yet another approach, in this case the γ-irradiation of a single crystal of [$^2H_6$]methylenecyclopropane.[49] At 77 K, this spectrum agreed in all ways with previously recorded spectra for TMM. Remarkably, however, when the sample was warmed to temperatures above 100 K (an experiment not previously essayed), a reversible loss of symmetry, from D_{3h} to C_{2v}, was observed in the ESR spectrum. This change was manifest in the appearance of a splitting in the *x* and *y* lines of the spectrum, and in the movement of the *z* lines (Fig. 2; additional evidence is provided in the spectrum from the all protio methylenecyclopropane, not reproduced here). The same behavior was observed for frozen solutions of [$^2H_6$]methylenecyclopropane in hexafluorobenzene and tetrahydrofuran,[49] suggesting that crystal packing/matrix effects are not responsible for the observed phenomenon. Dowd and Chow tentatively offered possible explanations of bond-stretch isomerism (transforming the high-symmetry $^3A_2'$ state to a lower symmetry $^3B_2$ state) or thermal population of an excited state triplet. Neither suggestion seems particularly plausible, however. Bond-stretch isomerism is nearly always an odious hypothesis (Dowd and Chow admitted it to be 'bizarre') and theory,[31,50,51] while not completely definitive, does not seem to allow for the presence of sufficiently low-energy triplet excited states (of whatever symmetry) to be populated. These spectral data continue to be especially puzzling.

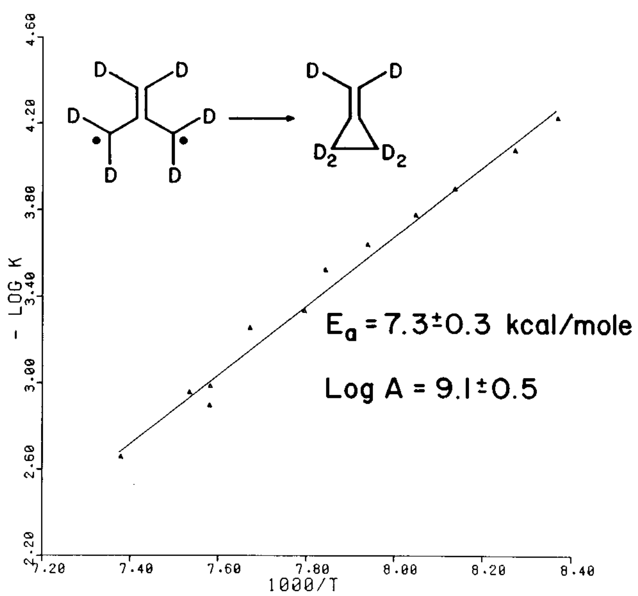


Fig. 3 Arrhenius plot of the kinetics of ring closure of [$^2H_6$]trimethylenemethane to [$^2H_6$]methylenecyclopropane. Reprinted with permission from *J. Am. Chem. Soc.*, 1977, **99**, 6438. Copyright 1977 American Chemical Society.

Activation barrier for disappearance of TMM. By following the loss of ESR signal intensity for TMM over various temperature ranges, Dowd and Chow[52,53] were able to construct Arrhenius plots indicating the activation energy for ring closure (to form methylenecyclopropane) to be about 7 ± 1 kcal mol^{-1} (Fig. 3). These experiments covered a temperature range from 113 to 137 K, and involved γ-irradiation of methylenecyclopropane either neat or highly concentrated in hexafluorobenzene glasses (2.8 to 4.8 M). The experiments showed no difference in the Arrhenius plots for methylenecyclopropane and [$^2H_6$]methylenecyclopropane, suggesting that tunnelling plays no role in the reaction rate for ring closure at these temperatures.

Similar experiments generating TMM from photolysis of 3-methylenecyclobutanone in several different solvents gave lower activation barriers, and led to activation energies and Arrhenius prefactors with a rather large amount of scatter. Dowd and Chow ascribed this poor reproducibility to some influence of the carbon monoxide fragment on the ring closure.[52,53]

The 7 kcal mol^{-1} barrier was assigned as the sum of the singlet–triplet splitting and any barrier (presumably very small) for ring closure from the singlet. It is, of course, also conceivable that the intersystem crossing takes place at some point along the ring closure coordinate where a decrease in separation between the two states offsets any energy increase in the triplet less than 7 kcal mol^{-1}. However, the former assignment was in conflict with then and subsequent theoretical studies,[29–31,50,51,54–61] all of which predicted the singlet to lie at least 14 kcal mol^{-1} or so above the triplet at the latter's equilibrium geometry (as do the PES results of Wenthold *et al.*[33] noted above). Feller *et al.*[58] examined the second possibility by following the experimental reports of Dowd and Chow with a reasonably thorough examination of a two-dimensional potential energy surface (the coordinates referring to rotation about two different C–C bonds) and continued to conclude that no pathway existed lower in energy than immediate state crossing followed by ring closure. Ma and Schaefer[61] repeated the work of Feller *et al.*[58] at higher levels of theory and came to a similar conclusion. Ma and Schaefer[61] additionally examined the influence of single molecules of coordinating species found in some of the experimental matrices (*e.g.*, carbon monoxide) on the ring-closure barrier. Although they found several coordinating species to lower the barrier

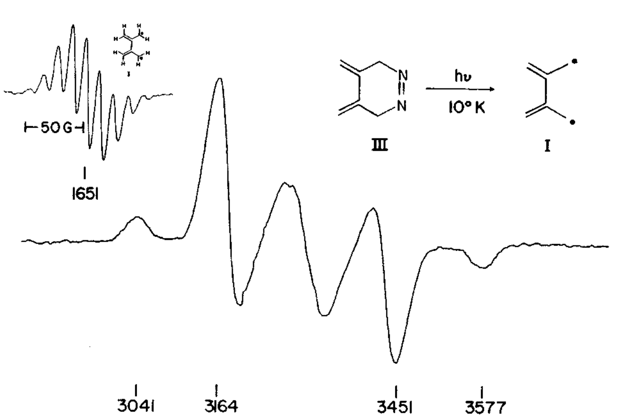


Fig. 4 ESR spectrum of tetramethyleneethane (I) from irradiation of III at 265 nm and 10 K. Shown here are the $\Delta m = 1$ and (inset) $\Delta m = 2$ lines. Reprinted with permission from *J. Am. Chem. Soc.*, 1986, **108**, 7416. Copyright 1986 American Chemical Society.

(relative to the triplet ground state) by a few tenths of a kcal mol^{-1}, they concluded that it was unlikely that this effect would be sufficiently large to explain the condensed-phase results.

This apparent discrepancy between theory and experiment has never been satisfactorily addressed. The experimental results span too broad a range of experimental conditions to be ignored. One tempting conclusion is that the disappearance of signal does not, in fact, correspond to ring closure, but Dowd and Chow cite studies indicating methylenecyclopropane to be indeed the observed product.[18,53] Platz[62] has pointed out that analogous kinetic experiments that measure the disappearance of ground-state triplet carbenes *via* singlet processes (*e.g.*, ylide formation) inevitably predict smaller S–T splittings than does theory—results along these lines from the Platz group are reported elsewhere in this issue for the case of 2,2,2-trifluoro-1-(4-methylphenyl)ethylidene.[63] It may be that more sophisticated dynamics studies on the theoretical side will be required to further address this question.

Ground states and geometries of parent and substituted TMEs. Dowd's most vexing challenges to the theoretical community, however, all involve TME. In 1986, reasoning that a different procedure to generate TME would provide additional weight to the prior experimental results (and potentially eliminate the persistent radical that had earlier required synthesis of the perdeuterio precursor, *vide supra*), Dowd *et al.*[64] prepared a new diazo precursor to TME (see Fig. 4) that on matrix photolysis extruded N_2 to generate the diradical. The ESR spectrum originally assigned to TME was reproduced in this experiment, and zfs values of $D = 0.025$ cm^{-1} and $E < 0.001$ cm^{-1} were observed (the discrepancy between this D value and the one reported[3] in 1970 was due to misinterpretation of the 1970 spectrum, which was identical with the 1986 spectrum). In addition, proton hyperfine coupling was observed in the $\Delta m = 2$ transition, and showed a nine-line pattern for eight equivalent protons (it is unclear whether the equivalence is accidental or arises from rapid rotation, but the latter seems unlikely since it would destroy allylic resonance). Finally, a Curie–Weiss plot of the intensity of this transition against $1/T$ showed linear behavior over the range 16–65 K.

These results have two important implications. First, the near (or exactly) zero value for E is consistent with the diradical having either D_{2h} or D_{2d} symmetry, *i.e.*, twist angles about the central C–C bond of 0 and 90 degrees, respectively (there is also, of course, the possibility that E is small at other torsion angles even though symmetry does not require it to be, however this would conflict with the situation observed for 2,3-dimethylenecyclohexa-1,3-diene as discussed below). Secondly, the linear Curie plot implies the triplet to be the ground state, or at least to lie no more than 10 cal mol^{-1} above the singlet. The latter observation conflicted with then published theory,[20,21] which predicted TME to be a ground state singlet [because in a disjoint non-Kekulé hydrocarbon one can have favorable singlet coupling between the two disjoint fragments (in this case allyl radicals) from interaction of negative spin densities at the central positions of the fragments; experimental confirmation of this analysis for a disjoint non-Kekulé system was subsequently demonstrated in the Yale laboratories of Professor J. A. Berson (whose contributions to the diradicals area parallel those of Dowd's) for other disjoint non-Kekulé systems[65]].

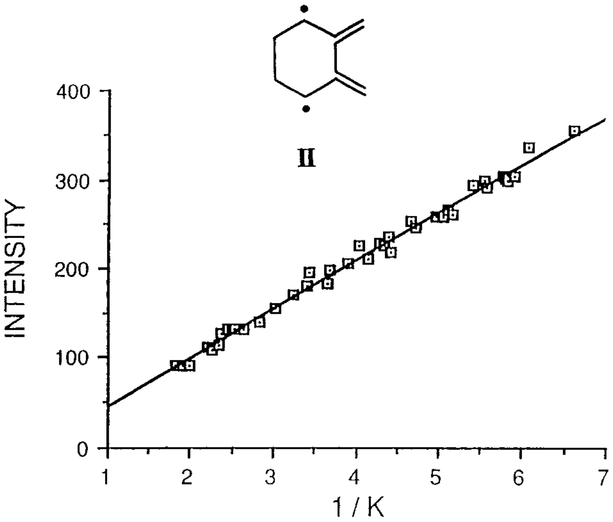


Fig. 5 Curie–Weiss plot (least squares, $r = 0.996$) of the signal intensity of the $\Delta m = 2$ line of the 2,3-dimethylenecyclohexa-1,3-diene diradical (**II**). The temperature range was 15–53 K; the solvent was 2-methyltetrahydrofuran. Reprinted with permission from *J. Am. Chem. Soc.*, 1987, **109**, 5284. Copyright 1987 American Chemical Society.

The geometry issue as it relates to the ESR spectrum is a particular puzzle. Subsequent theoretical studies at trustworthy levels all agree that triplet TME (a fairly trivial system since, unlike the singlet, the triplet wavefunction is dominated by a single Slater determinant) has a minimum-energy geometry at a twist angle of about 50 degrees.[66–69] At that geometry, Nachtigall and Jordan[68] found the triplet state to lie below the singlet using multireference configuration interaction (MRCI) methods. However, at D_{2h} or D_{2d} geometries (the latter being the singlet minimum) the singlet state was lowest in energy. So, unless the E zfs value is coincidentally near zero even for a twist angle of 50 degrees, it is difficult to reconcile the best theoretical results with experiment. Elsewhere in this issue, Clifford *et al.*[70] report on the photoelectron spectroscopy of the TME radical anion, and find (based on Franck–Condon analysis) that the theoretically predicted singlet and triplet structures agree well with the apparent gas phase geometries.

Never one to shrink from a challenge from the theoretical community, Dowd added more experimental data to the debate by pursuing two different paths. First, the geometry issue was addressed by preparing TME derivatives that tied together one end of each allyl unit into a ring. In 1987, Dowd *et al.*[71] prepared the six-membered ring derivative 2,3-dimethylenecyclohexa-1,3-diene diradical and demonstrated by a Curie plot that this system also was either a ground state triplet or had degenerate singlet and triplet states (Fig. 5). Interestingly, Matsuda and Iwamura[72,73] have since demonstrated the latter situation to be the case. With respect to the observed ESR spectrum of the triplet, Dowd *et al.* initially assumed the diradical to be a planar species based on molecular mechanics calculations. Shortly after publishing this work, however, Dowd took his first (published) advantage of the expertise of his colleague Jordan, and together they calculated the structure of the triplet species at the Hartree–Fock quantum mechanical level with a split-valence basis set.[74] This calculation revealed the twist angle between the two allyl units to be about 25 degrees. This result is consistent with the observation of zfs values of

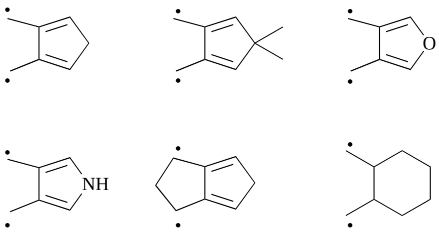


Fig. 6

$D = 0.024\ \mathrm{cm^{-1}}$ and $E = 0.0037\ \mathrm{cm^{-1}}$ for the triplet,[71] *i.e.*, an intermediate twist angle generates a non-zero E value. This would seem to be strong support for the contention that TME itself must have a triplet twist angle that is *not* intermediate between 0 and 90 degrees.

In 1987 Roth *et al.*[75] demonstrated that the five-membered ring analog of TME, 2,3-dimethylenecyclopenta-1,3-diene was also a ground state triplet (or has degenerate singlet and triplet states) based on Curie law behavior at low temperature. *Ab initio* calculations for this species predict a twist angle of zero degrees (*i.e.*, a planar diradical).[74,76] Additionally, the ground state of a furano analog of TME had been demonstrated to be the singlet by Zilm *et al.*[77] To explain these trends, Nash, Dowd, and Jordan[78] performed small MRCI calculations for these, TME, and four other analogous systems (Fig. 6), and showed that (*i*) the employed level of theory successfully predicted the correct ground state for all of the known systems (TME itself was restricted to planarity and predicted to have a singlet ground state at that geometry, a situation not really addressed by experiment but included for consistency with the other planar diradicals) and (*ii*) the calculated splittings correlated reasonably well (quadratically) with the restricted open-shell Hartree–Fock (ROHF) orbital energy splittings between the two SOMOs in the triplets (thereby providing in principle a simple method to predict S–T splittings in new TME derivatives). This analysis moreover provided a useful molecular orbital picture of how cyclic tethers connecting the two allyl units in TME permitted communication of spin *via* (hyper)-conjugative interactions.

Finally, in a separate effort to address the possibility that unresolved proton hyperfine coupling might broaden the x and y lines of the $\Delta m = 1$ transition in the ESR spectrum of TME and thereby obscure any splitting (such splitting would be diagnostic of a non-zero E zfs), Dowd *et al.*[79] prepared the perdeuterio derivative of the azo precursor used previously. The x and y lines in perdeuterio-TME, however, remained unresolved, thereby confirming the upper limit of $E < 0.001\ \mathrm{cm^{-1}}$ assigned previously.

To summarize the controversies remaining in this area, the geometry of triplet TME in the matrix remains to be established. The theoretical calculations are so simple that it is rather difficult to believe that they are incorrect about the preferred twist angle of roughly 50 degrees in the gas phase, and the PES results[70] are also consistent with this torsion. It may be that the E value in TME at this twist angle is coincidently near zero, but computational methods for predicting zfs parameters are insufficiently accurate to assess this possibility at the present time (Matsuda and Iwamura[72] cite unpublished calculations of E values for TME by Josef Michl, but in my opinion the cited values are equivocal). It may also be that the twist angle in triplet TME is affected by the matrix in the ESR experiments.

Of course, the ground state of TME is obviously tied to the issue of geometry and any possible matrix influences on the molecular geometries and state energies in the condensed-phase experiments. It is worth noting that the ground state may *change* as a function of torsion angle in the matrix (this might then explain the experimental Curie plot as arising from a metastable triplet—the PES results do not rule out such a coupling of the torsion angle and the ground state even for the gas phase). These points having been made, it seems clear that the S–T splittings at *all* relevant geometries will probably be rather small (less than ±2.0 kcal mol^{-1}), so that any controversy between theory and experiment will not be one of large magnitude, but will simply reflect the 'danger' of working near zero, where changes in sign make errors appear larger than they are.

Final remarks

Paul Dowd was a meticulous experimentalist whose careful measurements set a standard in the diradicals area. In the course of his career he expanded his interests, through collaboration with colleagues, into theory and gas-phase experiments. That career, tragically ended in 1996, generated a number of results that continue to pose important challenges to our understanding of non-Kekulé diradicals. The resolution of these issues remains to be accomplished, but assuming they are attacked by individuals with the same insatiable intellectual curiosity as I remember Paul having, no doubt such resolution will be achieved. I know Paul would have been pleased to acknowledge such achievements.

In closing this scientific summary of Paul's work, it seems appropriate to spend the last moment on a biographical note. I can think of no more succinct celebration of Paul's career than that offered by Professor William von Eggers Doering at his memorial service: '[Paul was a] magnanimous man of large spirit, in competition with secretive Nature, not with his colleagues, he was pleased by the fair songs of others; he was an all-too-rare bird in our cage. The loss of his presence at our meetings will be noted with sadness, but, more telling, with the realization that possibly none is either prepared or constituted to fill the gap.'

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