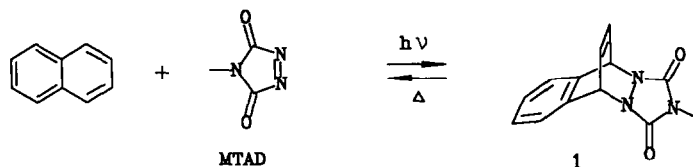


PHOTOCHEMICAL DIELS-ALDER ADDITION OF  
N-METHYLTRIAZOLINEDIONE TO PHENANTHRENE

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**Summary:** *Visible irradiation of solutions of N-methyltriazolinedione and phenanthrene results in several Diels-Alder type adducts. The mechanism for these photoadditions is discussed.*

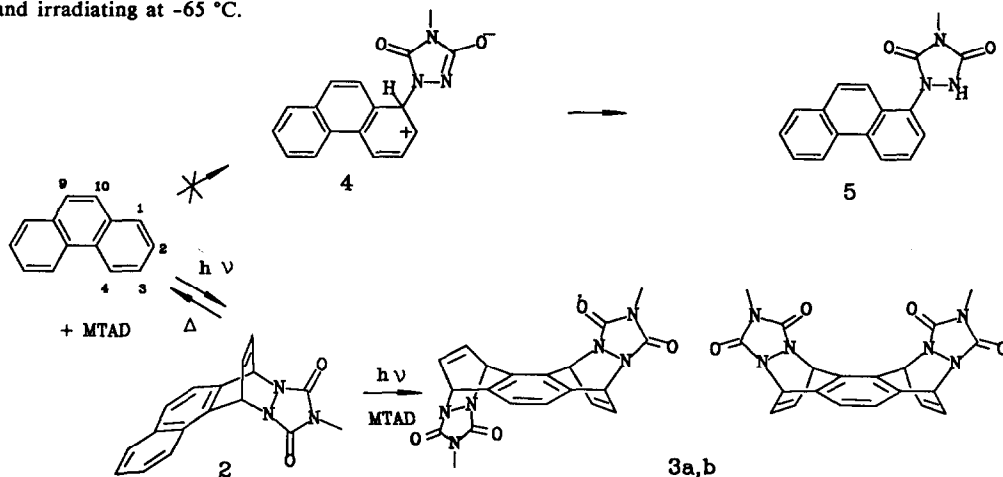
Triazolinediones (TADs) are powerful dienophiles.<sup>2</sup> TADs also give thermal [2+2], ene, and electrophilic additions to certain olefins and strained sigma bonds.<sup>3</sup> Addition products of TADs are of some interest as precursors to azo compounds, and hence to biradicals and other reactive molecules.<sup>2</sup> In contrast to thermal reactions, photoadditions of TADs have been little studied. We recently reported the photochemical cycloaddition of N-methyltriazolinedione (MTAD) to naphthalene to give 1.<sup>4</sup> Adduct 1 undergoes thermal cycloreversion with a half-life of ca. 12 h at room temperature. Through several steps, 1 was converted to a novel azo compound related to naphthalene, diazabenzosemibullvalene.<sup>5</sup> We now wish to report the photoaddition of MTAD to phenanthrene to give several [4+2] products. Analysis of the cycloaddition periselectivity lends mechanistic insight into these unusual photoadditions.



Visible-light irradiation of a solution of phenanthrene and MTAD ( $\text{CH}_2\text{Cl}_2$ , 0.02 M each, ca. 2h, room temperature) gave several cycloadducts, which could be separated by flash chromatography on silica gel. The  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ) of the first eluting product exhibited three doublets of doublets at 6.9 (2H,  $J=4.0, 3.2$  Hz), 6.7 (1H,  $J=4.0, 3.2$  Hz), and 6.0 (1H,  $J=4.0, 3.2$  Hz), and a singlet at 2.75 (3H) ppm. The aromatic protons were obscured by phenanthrene, which was always present with this adduct. This product was the most thermally labile, cleanly giving phenanthrene and MTAD at room temperature with a half-life of ca. 1 h. Based on the thermal chemistry of this product and the similarity of its NMR spectrum to that of 1, we assign it structure 2. The  $^{13}\text{C}$  NMR spectrum<sup>6</sup> is also consistent with this assignment.

Subsequent chromatography fractions contained two similar products that were only poorly separated, but which could be purified by recrystallization. NMR spectra indicate that both products comprise two MTAD molecules and one phenanthrene. Each product exhibits relatively simple  $^1\text{H}$  NMR spectra with one singlet in the aromatic region, an ABCD pattern in the olefin-bridgehead region, and one N-methyl singlet.<sup>6</sup> The  $^{13}\text{C}$  NMR spectra also indicate symmetric structures.<sup>6</sup> We assign these

products structures **3a,b**, formed from photoaddition of MTAD to **2**. The actual stereochemical assignment for **3a,b** remains undetermined. The bis-adducts **3a,b** are somewhat more thermally stable than mono-adduct **2**, giving phenanthrene and MTAD with a half-life of ca. 7 h at room temperature.  $^1\text{H}$  NMR spectra taken during the irradiations show that **2** grows in first, followed by **3a,b**.<sup>7</sup> Adduct **2** could be generated to the exclusion of the other products by increasing the ratio of phenanthrene to MTAD and irradiating at  $-65^\circ\text{C}$ .

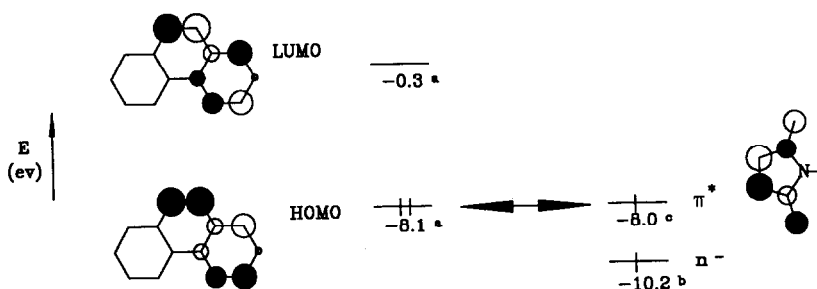


The photoaddition of MTAD to phenanthrene is striking. We know of no other thermal or photochemical 1,4-additions to phenanthrene. The photochemistry of phenanthrene has been studied extensively.<sup>8</sup> Excited-state phenanthrene (singlet or triplet) adds solely at the 9,10-positions to a number of olefins. The  $n,\pi^*$  singlet state of MTAD lies lower than the  $\pi,\pi^*$  of phenanthrene, however, and is the reactive state at the wavelengths of our irradiations. We wish to propose a simple explanation for the unusual regiochemistry observed with MTAD.

First, several points suggest that intermediates such as **4** are not involved in these additions. Similar intermediates have been proposed in MTAD additions to various dienes, and have been intercepted with methanol.<sup>3a</sup> Irradiation of phenanthrene and MTAD in acetic acid- $d_4$  still gives the mono- (**2**) and bis-adducts (**3a,b**) by NMR. Unless **4** is extremely short lived, we would expect that under these conditions it would be trapped. Moreover, electrophiles add predominantly to the 9-position of phenanthrene, with varying lesser amounts of 1- and 3-products observed depending on the reactivity of the electrophile. Although additions of radicals to phenanthrene have not been extensively studied, indications are that the 9-position is most reactive, as predicted by simple MO arguments.<sup>9</sup> It is thus not clear that excited MTAD would react selectively at the 1- or 4-positions of phenanthrene in a stepwise fashion, to the exclusion of the 9-position. Finally, we observe no products analogous to **5**, which might logically arise from intermediates such as **4** (particularly in acetic acid).

These results suggest concerted [4+2] addition of excited MTAD to phenanthrene. Although photochemical Diels-Alder reactions are at first sight forbidden by orbital symmetry, theoreticians have proposed mechanisms whereby these constraints might be relaxed in the case of very polar cycloadditions with substantial charge-transfer character.<sup>10</sup> Correlation diagrams indicate that if the dienophile has the lower energy excited state, then a [4+2] addition can be formally allowed in both the ground and excited states. The regio- and periselectivity of a number of photochemical cycloadditions have been

shown to be consistent with frontier orbital interactions between the half-filled MOs (SOMOs) of the excited partner with the corresponding HOMO and LUMO of the ground-state cycloaddend.<sup>9a</sup> In previously studied cases of excited-state phenanthrene additions, such as with maleic anhydride, these interactions fit the observed [2+2] adducts at the 9,10-positions.<sup>8</sup> In the case of excited MTAD, however, the orbital energetics favor interaction between the HOMO of phenanthrene and the highest SOMO of MTAD, as shown below.<sup>11</sup> The MOs have the correct symmetry for overlap at the 1,4-positions of phenanthrene, giving a stabilizing interaction on the excited-state surface at the geometry of the corresponding ground-state Diels-Alder transition state, leading eventually to 2. Others have invoked similar arguments to explain seemingly forbidden photoadditions.<sup>12</sup> It is interesting to note that Fukuzumi and Kochi have observed that highly polar Diels-Alder transition states have approximately the same energy as the corresponding radical ion pairs, which similarly suggests a close approach between ground and excited state surfaces at these geometries.<sup>13,14</sup>



- a) From IP and EA, ref. 11a. b) From IP, ref 11b. c) Determined from 0,0 uv transition.  
d) Approximate Huckel  $\pi$ -orbital coefficients shown.

We are continuing to explore the photoaddition of MTAD to other aromatic systems, and the conversion of the adducts to a variety of azo compounds.

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6. **2**  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  158.5, 158.3, 135.1, 133.9, 133.6, 133.4, 132.4, 128.7, 127.8, 127.6, 127.2, 126.2, 121.8, 121.6, 57.3, 52.8, 25.8 ppm. **3a**  $^1\text{H}$ NMR (300 MHz,  $d_6$ -DMSO)  $\delta$  7.38 (s, 2H Hz), 6.90 (t, 4H,  $J=2.6$  Hz), 6.50 (dd, 2H,  $J=3.0, 2.5$  Hz), 5.99 (dd, 2H,  $J=4.2, 2.4$  Hz), 2.79 (s, 6H) ppm;  $^{13}\text{C}$ NMR (75 MHz,  $d_6$ -DMSO)  $\delta$  157.9(2), 136.6, 133.6, 133.2, 131.7, 122.4, 56.3, 52.7, 25.3 ppm. **3b**  $^1\text{H}$ NMR (300MHz,  $d_6$ -DMSO)  $\delta$  7.28 (s, 2H), 6.83 (t, 4H,  $J=3.5$  Hz), 6.21 (t, 2H,  $J=3.9$  Hz), 5.86 (t, 2H,  $J=3.6$  Hz), 3.02 (s, 6H) ppm;  $^{13}\text{C}$ NMR (75 MHz,  $d_6$ -DMSO)  $\delta$  157.79, 157.78, 136.7, 133.2, 133.0, 132.0, 122.4, 56.2, 52.7, 25.3 ppm.
7. Longer irradiation times (>7 h) give in addition to **3a,b** another bis adduct, apparently formed by [4+2] cycloaddition of MTAD to the 1,4 and 9,12 positions of phenanthrene.  $^1\text{H}$ NMR (300MHz,  $\text{CDCl}_3$ )  $\delta$  7.60 (d, 1H,  $J=6.6$  Hz), 7.32 (m, 3H), 6.85 (dd, 1H,  $J=6.3, 0.9$  Hz), 6.78 (ddd, 1H,  $J=8.1, 5.7, 1.2$  Hz), 6.63 (ddd, 1H,  $J=8.1, 5.5, 1.4$  Hz), 6.56 (dt, 1H,  $J=5.4, 1.2$  Hz), 5.81 (d, 1H,  $J=6.3$  Hz), 5.39 (dd, 1H,  $J=5.4, 1.2$  Hz), 3.03 (s, 3H), 2.71 (s, 3H) ppm;  $^{13}\text{C}$ NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  24.9, 25.2, 51.3, 51.6, 57.2, 63.8, 121.5, 123.0, 126.5, 127.8(2), 128.0, 129.6, 132.6, 135.8, 140.4, 157.0, 157.3 ppm.
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