79396-24-0; **2e**, 78907-25-2; **3a**, 88158-10-5; **3b**, 88158-11-6; **3c**, 4552-61-8; **3d**, 79384-30-8; **3e**, 78907-22-9; **4c**, 88158-12-7; **4d**, 88158-13-8; **5a**, 88158-14-9; **5b**, 88158-15-0; **6a**, 88158-16-1; **6b**, 88158-17-2; **6d**, 88158-18-3; guanosine, 118-00-3; *p*-methylbenzyl bromide, 104-81-4; *p*-nitrobenzyl bromide, 100-11-8; *p*-chlorobenzyl iodide, 35424-56-7; sodium *p*-chlorobenzylate, 60812-71-7; sodium *p*-methylbenzylate, 71190-75-5; 2-amino-6-chloropurine riboside, 2004-07-1; *p*-chlorobenzyl chloride, 104-83-6; *p*-methylbenzyl chloride, 104-82-5; 7-methylguanosine, 20244-86-4; 7-ethylguanosine, 71369-24-9.

Interaction between Triple Bonds in 1,8-Diethynylnaphthalenes

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The He(I) photelectron spectra of the alkyl-substituted 1,8-diethynylnaphthalenes **2**–**5** are reported. The comparison between experimental data and the results of MINDO/3 calculations indicates that the energy split between the molecular orbitals derived from the linear combinations of the acetylenic in plane π orbitals is essentially a function of their spatial separation.

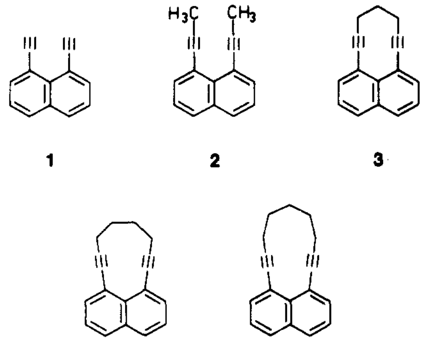
1,8-Diethynylnaphthalene (**1**,[1] Chart I) and its alkyl derivatives **2**–**5**[2] are interesting model compounds to study the mutual interaction of two acetylenic moieties. As has been shown by X-ray studies,[3,4] the triple bonds of these compounds are fixed by the naphthalene frame and the chain at a distance of about 3 Å. Our recent studies on 1-ethynylnaphthalene, 1,5-diethynylnaphthalene, and **1**[5] demonstrated that He(I) photoelectron (PE) spectroscopy is ideally suited to probe the interaction in **1**–**5**.

Model Considerations

Before discussing the PE spectra, we will use the concepts of through-space and through-bond interaction[6] to analyze the effects prevailing in **1**–**5**.

Consider two acetylenic units arranged parallel to each other as shown in the middle of Figure 1. The overlap between the π clouds will cause a different interaction for the "in plane" (π_i) and "out of plane" (π_o) orbitals since the in plane overlap is of $2p_\sigma$–$2p_\sigma$ type and thus considerably larger at distances around 3 Å than the out of plane $2p_\pi$–$2p_\pi$ overlap. The corresponding interaction diagram is shown in Figure 1.

Chart I



1 **2** **3** **4** **5**

Table I. Ionization Energies of the Compounds **1**–**5**[a]

peak no.	compd 1	2	3	4	5
1	7.88	7.48	7.53	7.50	7.48
2	8.99	8.6	8.5	8.6	8.5
3	9.31	8.7	8.7	8.7	8.6
4	9.49	8.9	8.8	8.9	8.8
5	10.27	9.8	9.78	9.8	9.7
6	10.82	10.0	10.4	9.9	9.8
7	11.15	10.7	10.7	10.6	10.6

[a] All values are in electron volts.

Table II. Orbital Energies (eV) of the Six Highest Occupied Orbitals of **1**–**5** Using the MINDO/3 Method[a]

irreducible representation	compd 1	2	3	4	5
$3a_2$ (π)	−7.94	−7.83	−7.83	−7.83	−7.83
$4b_2$ (π)	−8.89	−8.89	−8.87	−8.86	−8.86
$3b_2$ (π)	−9.37	−9.10	−9.03	−9.09	−9.10
$12b_1$ (π_i^-)	−9.33	−9.05	−8.51	−8.91	−8.99
$12a_1$ (π_i^+)	−10.44	−9.91	−10.19	−9.83	−9.82
$2a_2$ (π)	−10.63	10.27	−10.40	−10.21	−10.22

[a] The irreducible representations refer to compound 1 (C_{2v}).

The energy levels of the bonding ($\epsilon(\pi_i^+)$) and antibonding ($\epsilon(\pi_i^-)$) linear combinations of two acetylenic π systems have been obtained by MINDO/3[7] calculations. In Figure 2 these orbital energies as well as their difference, Δ, are plotted against the distance between the two triple bonds. Besides the through-space interaction of the two acetylenic moieties in **1**–**5**, the through-bond interaction with the σ frame must be taken into account. The influence of the naphthalene fragment has been estimated by comparison of the PE spectra of **1** and 1,5-diethynylnaphthalene.[5] In the following discussion we assume this influence to be similar in all compounds. The influence of the bridges, however, is different. Consider Figure 3. On the left side of this figure is indicated the highest occupied σ orbital of the isolated tetramethylene bridge

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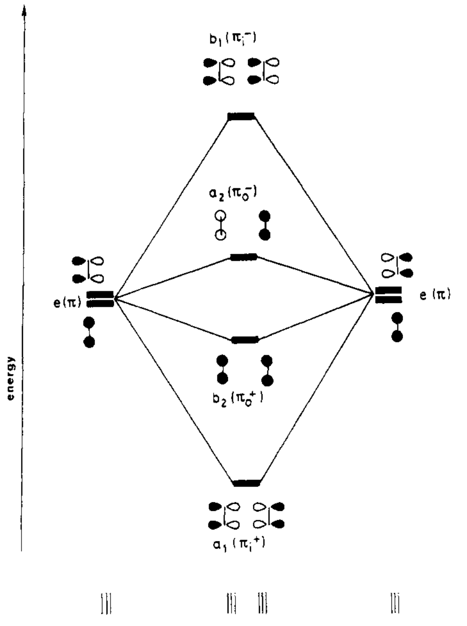

Figure 1. Qualitative interaction diagram of two acetylenes parallel to each other in a common plane. The symbols π_0 and π_i denote the "out of plane" and "in plane" π orbitals.

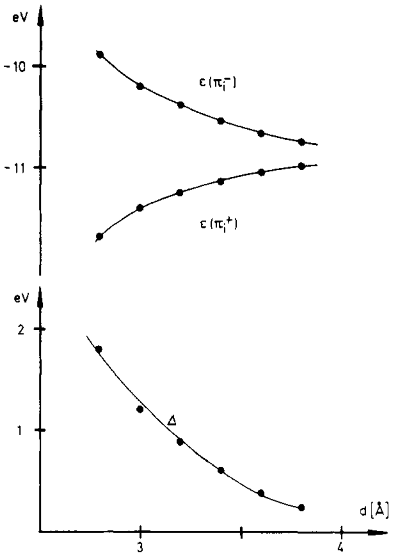

Figure 2. (a) Orbital energies (MINDO/3) for the symmetric (π_i^+) and antisymmetric (π_i^-) in plane linear combinations of two acetylenes as a function of the distance d. (b) Energy difference $\Delta = \epsilon(\pi_i^-) - \epsilon(\pi_i^+)$ as a function of the distance d.

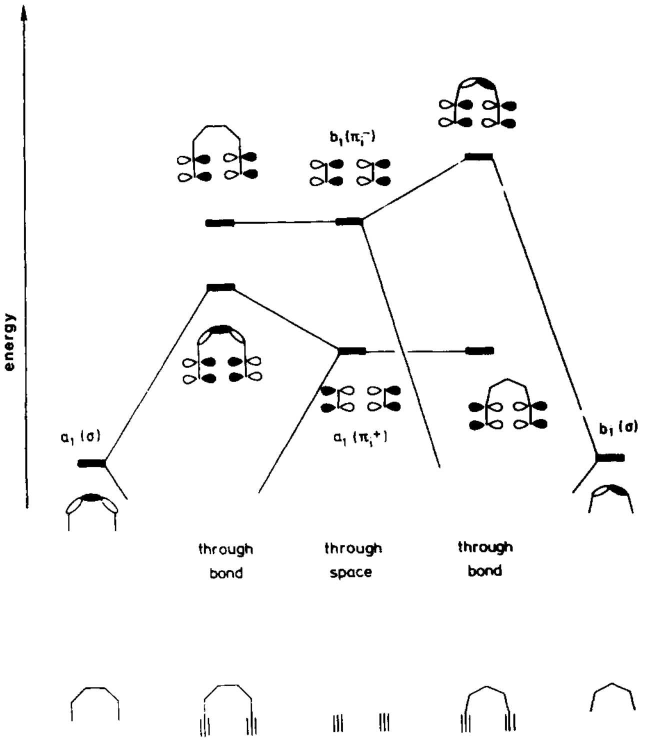

Figure 3. Qualitative interaction diagram between two acetylene moieties, a $(CH_2)_2$, and $(CH_3)_3$ σ fragment.

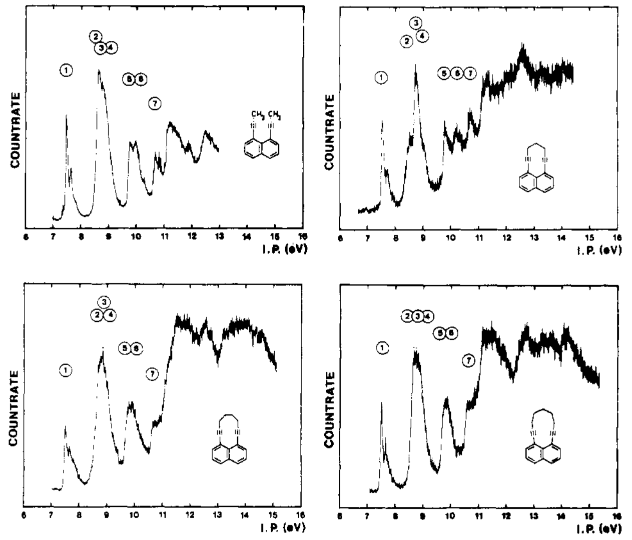

Figure 4. PE spectra of **2**–**5**.

in **4**. This orbital is symmetrical with respect to a plane of symmetry perpendicular to the molecular plane. On the right side the highest occupied σ orbital of the trimethylene bridge in **3** is shown which is antisymmetrical with respect to the mirror plane described above. The irreducible representations refer to C_{2v} symmetry. As a consequence of the different point group of the bridge orbitals we expect a different interaction pattern for the "in plane" linear combinations π_i^+ and π_i^-. The anticipated interaction diagram is shown in Figure 3.

PE Spectra of 2–5

The method of choice to study the interaction patterns between the π MO's of **2**–**5** is photoelectron (PE) spectroscopy with a He(I) light source. Under the assumption of the applicability of Koopmans' theorem ($I_{v,j} = -\epsilon_j$) the measured vertical ionization energies ($I_{v,j}$) can be correlated with the calculated orbital energies (ϵ_j). A large number of investigations have shown that this assumption is valid for most organic molecules.

The PE spectra of **2**–**5** are shown in Figure 4; in Table I the measured vertical ionization energies are collected together with those obtained for **1**.[5] In Table II the orbital energies obtained by MINDO/3[7] calculations on **1**–**5** are given. The irreducible representations are those obtained for **1** considering the valence electrons only and assuming C_{2v} symmetry. The highest occupied MO's of **1** are shown schematically in Figure 5.

The spectra of **2**, **4**, and **5** are very similar. In the region between 7 and 10.5 eV we find three bands with the intensity ratio 1:3:2. We assign these bands as being due to one, three, and two ionization processes, respectively. The spectrum of **3** is significantly different from those of the other compounds.

The second peak shows a shoulder at 8.5 eV and the peaks five and six are clearly separated.

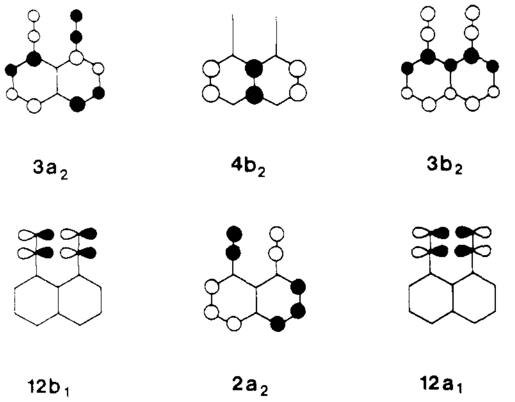

Figure 5. Schematic drawing of the highest occupied MO's of **1**.

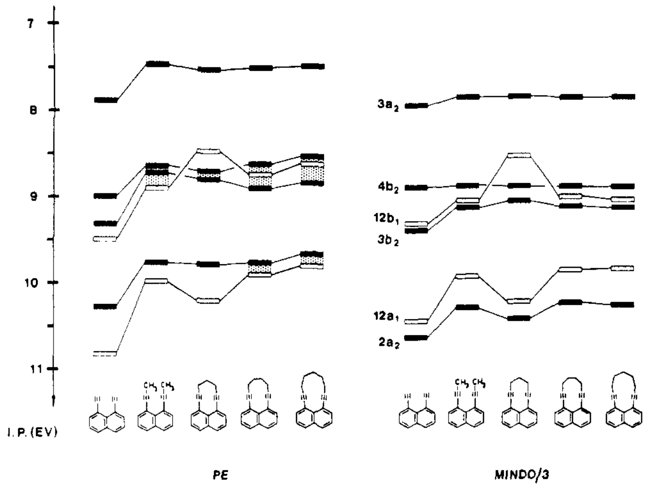

Figure 6. Correlation diagram between the first PE bands of **1**–**5** (left) and between the highest occupied MO's of **1**–**5** (right). The irreducible representations refer to **1**. The full bars were used for the "out of plane" π MO's while the open bars denote the "in plane" π MO's.

To interprete the PE spectra of **2**–**5** it is instructive to consider first that of **1**. The spectrum of this compound has recently been assigned by comparison with those of 1-ethynyl- and 1,5-diethynylnaphthalene. The assignment was supported by the results of MINDO/3 calculations.[5]

Although MINDO/3 reproduces quite reasonably the geometry and orbital energies, the π_i levels ($12b_1$ and $12a_1$) are placed at energies that are too high, a shortcoming encountered frequently.

Keeping in mind this shortcoming and the given assignment of **1**, we are now ready to interprete the PE spectra of **2**–**5**. A comparison of the experimental data with the orbital sequence obtained by the MINDO/3 method is shown in Figure 6. We find a very close resemblance of experiment and calculation, except that $12a_1$ is found at too high an energy.

For the first bands of **1** and **2** we encounter a shift of 0.5–1.0 eV due to the electron-donating capability of the methyl groups. This effect is smaller for the second band since $4b_2$ has nodes going through the 1- and 8-positions of the naphthalene ring (see Figure 5).

In the case of **3** we expect an increase of the through-space effect between the two acetylene π systems due to the decrease of the distance and a destabilization of $12b_1$ (π_i^-) due to the through-bond interaction with the aliphatic bridge (see Figure 3). As can be seen from Figure 6 this assumption is supported by the PE spectrum; the splitting in energy between $12b_1$ (π_i^-) and $12a_1$(π_i^+) is considerably larger in the case of **3** compared with that of **2**.

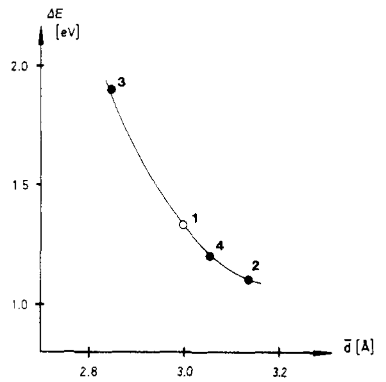

Figure 7. Energy difference (ΔE) between the bands assigned to $12b_1$ (π_i^-) and $12a_1$ (π_i^+) of the PE spectra of **1**–**4** as a function of the average distance ($\bar{d}$) between the acetylenic moieties.

When going from **3** to **4** we anticipate just the opposite trend. We assume a smaller through-space effect due to the increase of the average distance between the two acetylenic fragments and a destabilization of $12a_1$ (π_i^+) caused by the through-bond effect of the tetramethylene bridge.

In the case of **5** we expect that the longer methylene chain increases the distance between the two triple bonds. Thus a smaller through-space interaction of the π_i orbitals should result (see Figures 2 and 3). On the other hand, the odd number of methylene groups implies a through-bond interaction similar to that prevailing in **3** (see Figure 3) which enlarges the energy gap between π_i^+ and π_i^-. As a result, we may expect an approximate cancellation of both effects. This expectation is confirmed by the MINDO/3 results which predict the same split between $12a_1$ and $12b_1$ for **4** and **5**. Due to the strong overlap of the PE bands 2–4 and 5 and 6, these predictions cannot be verified experimentally.

Conclusions

The MINDO/3 results reproduce quite well the observed band pattern for the PE spectra of **1**–**5**. The slightly different appearance of the spectrum of **3** can be explained in terms of a relatively large splitting of the π_i^+ and π_i^- levels for this species.

In Figure 7 we have plotted the observed energy split, ΔE, between π_i^+ and π_i^- as a function of the average distance between the acetylenic moieties. For **2**–**4** we used X-ray data;[3,4] in the case of **1** the geometry predicted by MINDO/3 was employed. The similarity between Figure 7 and that of Figure 2b is obvious. We conclude from this similarity that the through-space interaction in **1**–**5** dominates strongly.

Experimental Section

Compound **2** has been prepared according to the literature.[2] Compounds **3**–**5** were given to us by Prof. H. A. Staab.[2] The PE spectra of the pure material have been recorded on a PS 18 spectrometer from Perkin-Elmer (Beaconsfield, England). The calibration was done with Ar and Xe.

Acknowledgment. We are grateful to Prof. H. A. Staab for providing us with a sample of **3**–**5**. Financial support from the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the BASF Aktiengesellschaft is gratefully acknowledged.

Registry No. **1**, 18067-44-2; **2**, 22360-77-6; **3**, 32137-40-9; **4**, 32137-39-6; **5**, 87842-94-2.