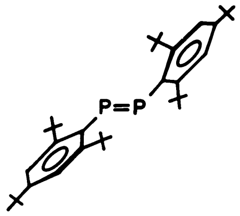
CHEMISTRY LETTERS, pp. 313 - 316, 1984.

PHOTOELECTRON SPECTRA OF DIARYLDIPHOSPHENES

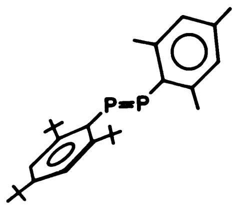
Rolf GLEITER,* Gert FRIEDRICH, Masaaki YOSHIFUJI,†* Katsuhiro SHIBAYAMA,†
and Naoki INAMOTO†
Institut für Organische Chemie der Universität Heidelberg,
D-6900 Heidelberg, West-Germany
†Department of Chemistry, Faculty of Science, The University of
Tokyo, Hongo, Tokyo 113

The He(I) photoelectron (PE) spectra of bis(2,4,6-tri-t-butylphenyl)diphosphene and mesityl(2,4,6-tri-t-butylphenyl)diphosphene are reported. An interpretation based on semiempirical calculations and comparison with other data is suggested.

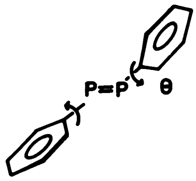
Recently it was demonstrated that diphosphenes can be prepared and isolated if the substituents are very bulky.[1-4] This synthetic progress allows us to study the physical and chemical properties of this class of compounds. To contribute to the question of bonding in diaryldiphosphenes we have analyzed the He(I) photoelectron (PE) spectra of E-bis(2,4,6-tri-t-butylphenyl)diphosphene (1)[1,5] and mesityl-(2,4,6-tri-t-butylphenyl)diphosphene (2).[2]



1



2



3

Figure 1 shows the PE spectrum of 1. The data obtained from 1 and 2 are collected in Table 1. The PE spectra of 1 and 2 are quite similar and show three peaks below 10 eV (bands ① - ④) followed by a shoulder (band ⑤) and a big structureless band, typical for t-butyl groups. The PE bands in 2 are less pronounced than in 1, probably due to the higher flexibility of 2 compared with 1. To assign the PE spectra we proceeded in two ways: first the spectra of 1 and 2 were compared with the results obtained for arylphosphines, as have been described in a series of phenyl, p-tolyl, and p-t-butylphenyl derivatives,[6] and secondly using Koopmans' approximation

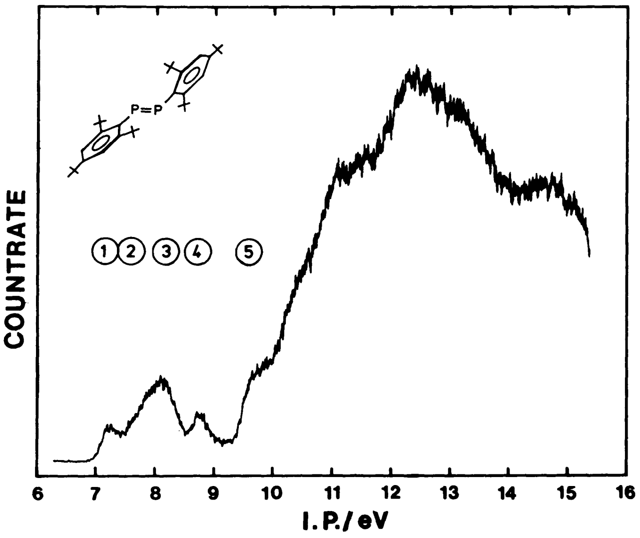


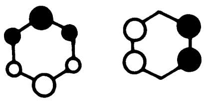
Fig. 1. He(I) PE spectrum of 1.

Table 1. Comparison of Obsd $I_{v,j}$(1 and 2) and Calcd $-\varepsilon_j$(3)

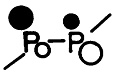
Band	$I_{v,j}$(1)/eV	$I_{v,j}$(2)/eV	$-\varepsilon_j$(3)/eV MINDO/3	$-\varepsilon_j$(3)/eV MNDO
①	7.23	7.8	7.38 ($11a_g$, n_-)	9.02 ($11a_g$, n_-)
②	7.6	8.1	8.92 ($10b_u$)	9.58 ($6b_g$)
③	8.1	8.4	9.09 ($7a_u$, π)	9.58 ($7a_u$, π)
			9.17 ($6b_g$)	9.76 ($10b_u$)
			9.17 ($6a_u$)	10.28 ($6a_u$)
④	8.7	9.4	9.34 ($10a_g$)	10.61 ($10a_g$)
⑤	9.75	10.05	10.39 ($9b_u$, n_+)	12.35 ($9b_u$, n_+)

($I_{v,j} = -\varepsilon_j$),7) the measured vertical ionization energies, $I_{v,j}$, were approximated by the calculated orbital energies, ε_j, for the ground state. This assumption implies small and about equal energy defects caused by electron correlation and relaxation during ionization. To derive the orbital energies we used the MINDO/3 model8) with modified P, C parameters9) and the MNDO procedure10) which have been proved to be quite reliable in the case of phosphorus compounds.11)

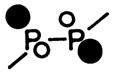
The comparison with the PE-results of arylphosphines6) leads to the following expectations: a) four closely situated transitions arising from the linear combinations of the e_{1g} orbitals of benzene shown below together with the two lone pairs on the phosphorus atoms and the π-orbital on the P_2 unit; b) about equal shifts of the "lone-pair-bands" and "π-bands" on replacing the t-butyl groups in 1 by methyl or hydrogen. These expectations are met by the PE results shown in Table 1 if we adopt the suggested assignment.



e_{1g}



$b_u(n_+)$



$a_g(n_-)$

With these expectations in line are the results of MO calculations on diphenyldiphosphene (3) assuming C_{2h} symmetry ($\theta = 90°$). In Table 1 the results of a MINDO/3 and MNDO-calculation are listed.[12] Although the predicted sequence differs somewhat, both results agree in the following points:

1) The antibonding linear combination of the lone-pairs ($11a_g(n_-)$) is predicted to be the HOMO.
2) The four π-orbitals ($10b_u$, $6b_g$, $6a_u$, and $10a_g$) (see Fig. 2) are predicted to be closely situated next to $7a_u$, the π-orbital of the P-P double bond.
3) The energy difference between $11a_g(n_-)$ and $9b_u(n_+)$ is predicted to be 3 eV (MINDO/3) and 3.3 eV (MNDO), respectively. These results agree with ab initio calculations (44-31G basis) on H_2P_2 which predict 3.5 eV.[13]

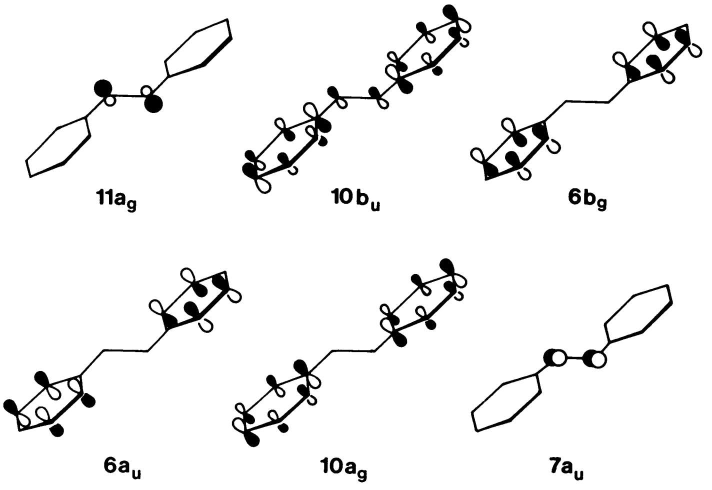


Fig. 2. Schematic drawing of the highest occupied molecular orbitals of 3.

Based on these considerations and results we assigned the first band to $11a_g$, the bands ② - ④ to five transitions $10b_u$ to $10a_g$, and the band ⑤ to $9b_u$. With this assignment the intensities of the corresponding peaks are reasonable. Furthermore the low intensity of the first band in the electronic spectra of 1 and 2 1,2) ($b_g(\pi^*) \leftarrow a_g(n)$) favors the assignment of 11a_g to the HOMO. The assignment must be, however, tentative and the assignment of the exact position of 7$a_u(\pi)$ and 9$b_u(n_+)$ must be reserved to further investigations including studies on aliphatic diphosphenes.

The PE spectra of 1 and 2 were recorded on a PS 18 spectrometer (Perkin Elmer Ltd., Beaconsfield, England) using a heated probe. The spectra were calibrated using Ar and Xe.

We are grateful to the Fonds der Chemischen Industrie, the Deutsche Forschungsgemeinschaft, the BASF Aktiengesellschaft, Ludwigshafen, and the Scientific Research Grant-in-Aid of the Ministry of Education, Science and Culture of Japan (No. 57540276) for financial support. Thanks are due to A. Flatow for the PE measurements and Dr. K. Hirotsu and Dr. T. Matsushita for helpful discussions on the structure of 1.

References

1) M. Yoshifuji, I. Shima, N. Inamoto, K. Hirotsu, and T. Higuchi, J. Am. Chem. Soc., 103, 4587 (1981); 104, 6167 (1982).
2) M. Yoshifuji, K. Shibayama, N. Inamoto, T. Matsushita, and K. Nishimoto, J. Am. Chem. Soc., 105, 2495 (1983).
3) C. Couret, J. Escudié, and J. Satgé, Tetrahedron Lett., 23, 4941 (1982).
4) A. H. Cowley, J. E. Kilduff, T. H. Newman, and M. Pakulski, J. Am. Chem. Soc., 104, 5820 (1982).
5) Preliminary PE data for 1 have been mentioned in: B. Çetinkaya, P. B. Hitchcock, M. F. Lappert, A. J. Thorne, and H. Goldwhite, J. Chem. Soc., Chem. Commun., 1982, 691.
6) M. A. Weiner, M. Lattman, and S. O. Grim, J. Org. Chem., 40, 1292 (1975); H. Bock, Pure Appl. Chem., 44, 343 (1975); D. E. Cabelli, A. H. Cowley, and M. J. S. Dewar, J. Am. Chem. Soc., 103, 3286 (1981) and references therein.
7) T. Koopmans, Physica (The Hague), 1, 104 (1933).
8) R. C. Bingham, M. J. S. Dewar, and D. H. Lo, J. Am. Chem. Soc., 97, 1285 (1975); P. Bischof, ibid., 98, 6844 (1976).
9) G. Frenking, H. Goetz, and F. Marschner, J. Am. Chem. Soc., 100, 5295 (1978).
10) M. J. S. Dewar and W. Thiel, J. Am. Chem. Soc., 99, 4899 (1977).
11) R. Gleiter, M. C. Böhm, and M. Baudler, Chem. Ber., 114, 1004 (1981); R. Gleiter, M. C. Böhm, M. Eckert-Maksić, W. Schäfer, M. Baudler, Y. Aktalay, G. Fritz, and K.-D. Hoppe, ibid., 116, 2972 (1983).
12) For our model calculations on 3 we minimized the heat of formation with respect to the P-P and P-C distances as well as for θ.
13) T. Matsushita and K. Nishimoto, private communication.

(Received November 1, 1983)