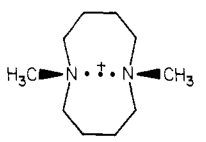
outside protonation which occurs with such reluctance.

The $D(N^+{-}H)$ values for **6** and **9** are exceptionally low. As discussed in the introduction, Staley and Beauchamp suggested[8] that comparison of $D(N^+{-}H)$ values for **1** and **4** provided a direct measure of the resonance stabilization of the radical cation from **4** (by through-bond coupling in this case). According to the values in Table II, this amounts to 9 kcal mol$^{-1}$. Application of the Staley–Beauchamp argument to the pairs **2**/**6** and **3**/**9** leads to estimated stabilization energies of 11 kcal mol$^{-1}$ for both $\mathbf{6}^{+\cdot}$ and $\mathbf{9}^{+\cdot}$, presumably by through-space interaction. This argument however relies on the strain energies of the monoprotonated ions of the mono- and diamines being the same. As we have argued above, this is probably not the case, the monoprotonated ions of the *mono*amines being more strained. This means that the estimated stabilization energies are too small, perhaps by 1–3 kcal mol$^{-1}$ for $\mathbf{6}^{+\cdot}$, but by perhaps as much as 10 kcal mol$^{-1}$ for $\mathbf{9}^{+\cdot}$. A better model for **9** would probably be the inside CH isomer of **3**, which is unknown at present.

Recently the kinetics of decomposition of the radical ion **11** were studied.[22] The rate-limiting step is probably cleavage of the 3-electron $\sigma$ bond. The free energy of activation for this process (14.5 kcal mol$^{-1}$) is therefore a reasonable estimate of the bond dissociation energy for the 3-electron $\sigma$ bond, since the reverse process probably has no activation energy. There seems to be encouraging semiquantitative agreement on the strengths of the 3-electron $\sigma$-bonding interaction in **6**, **9**, and **11**.



11

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# The First Bis Gem Donor–Acceptor Substituted Allene: Synthesis, Geometry, and Electronic Structure

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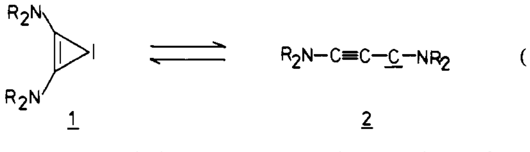
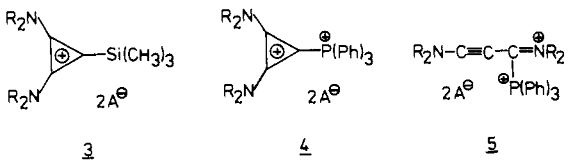
**Abstract:** The synthesis of 1,3-bis(dimethylamino)-1,3-bis(triphenylphosphonio)allene diiodide (**12**), the first bis gem donor–acceptor substituted allene, is reported. the X-ray structure of this salt shows geometrical features such as a twist toward a trans planar geometry and tilt of the $Ph_3P^+CNMe_2$ units, which are reproduced by MNDO calculations on the 1,3-diamino-1,3-diphosphonioallene dication. Strong interactions between the allene $\pi$ orbitals, the $\sigma^*_{CP}$ orbitals (negative hyperconjugation), and the amine lone pairs are responsible for the geometric distortions.

During investigations on the generation and reactions of nucleophilic cyclopropenylidenes[3] **1**, we became interested in the isomeric nucleophilic propargylene **2**—a hitherto unknown species. In particular, we were intrigued by the possibility that these two (singlet) species might be connected by a carbene–carbene rearrangement, (1). For clarification of this question, generation



1 2 (1)

of **2** from some open-chain precursors was indicated. In view of the successful generation of **1** from precursors **3** and **4** by F$^-$

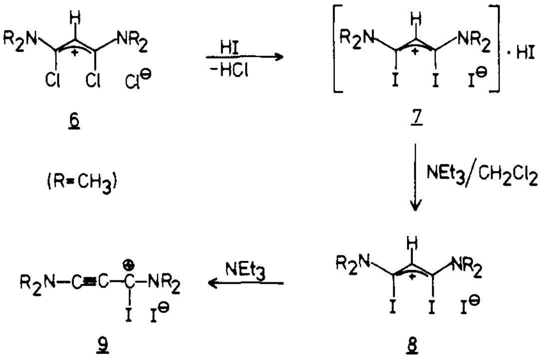


3 4 5

induced $\alpha$-elimination,[3,4] we felt that a phosphonium salt, **5**, would be a suitable precursor for **2** by analogy. In this paper we report on the attempted synthesis of such a propargylene precursor which resulted in the formation of an allene with novel structural features.

**Synthesis of a Stable Propargyl Salt.** A conventional synthesis of the dication salt **5** necessitates generation of a halopropargyl salt and its subsequent reaction with triphenylphosphine. We were able to obtain for the first time a stable, isolable propargyl salt by the strategy shown in Scheme I. When the easily available[5]

Scheme I



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(1) University of Erlangen.

(2) Technical University of Munich.

(3) (a) Weiss, R.; Wolf, H.; Priesner, C. *Angew. Chem.* **1978**, *90*, 486. Weiss, R.; Hertel, M.; Wolf, H. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 473.

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cyanine salt **6** was treated with excess dry gaseous HI in $CH_2Cl_2$, a complete chlorine–iodine exchange took place and an additional mole of HI was added to the primary product to give the yellow $CH_2Cl_2$-insoluble salt **7**. The precise structure of this salt is unknown at present, but according to IR evidence the organic cation in **7** is of lower symmetry than the one in **6**. This suggests protonation of one of the dimethylamino groups by HI. Pure **8** is liberated from **7** by 1 equiv of $NEt_3$ in almost quantiative yield. This reaction takes several hours at ambient temperatures, as both **7** and **8** are only slightly soluble in $CH_2Cl_2$. **8** is an air-stable salt, which can be almost quantitatively converted into the iodopropargyl salt **9** by excess $NEt_3$. **9** can be precipitated from $CH_2Cl_2$ solution by $Et_2O$ as air-stable yellow crystals.

The structure of **9** follows from the analytical data in conjunction with the following spectroscopic data: (1) in the IR spectrum the triple bond is indicated by an intense split band at 2130 $cm^{-1}$; (2) the $^1H$ NMR spectrum shows two different $N(CH_3)_2$ groups, the one at lower field appearing as a doublet, due to rotational hindrance. The latter signal probably corresponds to the $N(CH_3)_2$ group attached to the iodine-carrying C atom.

To our knowledge **8** and **9** represent the first examples—albeit heavily donor-stabilized ones—of the hitherto unknown[6] iodocarbenium ions. Iodine seems to exert a remarkable stabilizing effect (probably of the +I type) on carbenium ions of this type. Thus, for instance, **8** is moisture insensitive and quite generally fairly unreactive toward nucleophiles, whereas the chlorine counterpart **6** reacts rapidly with nucleophiles of all kinds. Similarly, the thermal and air stability of **9** contrasts sharply with our failure to synthesize its chlorine counterpart by base-induced dehydrochlorination of **6**. These observations are in conflict with current belief that in solution the carbenium ion stabilizing capacity of the halogens decreases in the order F > Cl > Br > I.[6] It is noteworthy, however, that gas-phase experiments indicate precisely the reverse order of carbenium ion stabilization by halogens in $CH_2X^+$ (X = F, Cl, Br, I)[7] and that this latter sequence has found support in recent calculations.[8]

Our present qualitative findings are inconclusive in this respect. This arises because of the intriguing possibility of cation–anion contacts in both **8** and **9** via n–$\sigma^*$ contacts of type **10**.

**10**

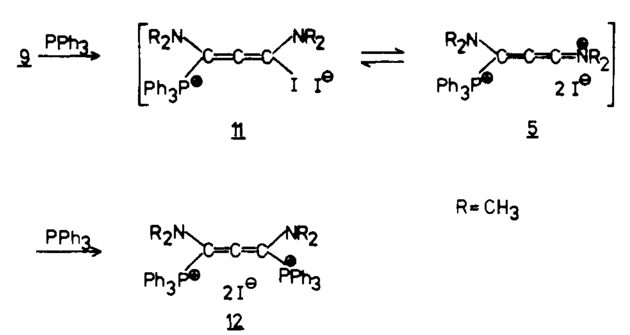
An intermediate of this type has recently been invoked in the photochemical generation of $CH_2$ from $CH_2I_2$.[9] The bonding situation in **10** is reminiscent of the one in trihalides $X_3^-$ and represents a characteristic point on the reaction coordinate associated with $\alpha$-elimination of $I_2$ and formation of the underlying (singlet) carbene.

One of the consequences of this bonding mode would be a reduced electrophilicity of the $\pi$ system in both **8** and **9** in comparison to analogous systems with innocent counterions like $ClO_4^-$, $BF_4^-$, etc.

Thus, we cannot yet judge whether the remarkable stability of both **8** and **9** is due to a strong inherent carbenium ion stabilizing effect of iodine, to a cation–anion interaction of type **10**, or to both effects. Conductivity measurements on **8** and **9**, ideally in conjuction with X-ray investigations, could resolve this interesting question.

**Synthesis of a Bis Geminally Donor–Acceptor Substituted Allene.** In an attempt to generate a dication salt of type **5**, **9** was reacted with $PPh_3$ in $CH_2Cl_2$. However, the only reaction product which was formed in high yield (90%) contained an additional mole of $PPh_3$ and was shown to be the novel allene **12** by analytical, spectroscopic, and X-ray data. This salt is probably formed as shown by Scheme II.

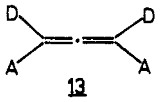
Scheme II



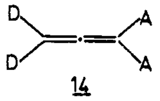
For steric reasons nucleophilic attack of $PPh_3$ on **9** should take place at the allenyl position, giving rise to the intermediate **11**, which in turn could be in equilibrium with **5**. Obviously this latter species is too electrophilic to be stable under the reaction conditions. Neither **11** nor **5** could be observed spectroscopically; even if **9** was used in large excess **12** remained the only observable product.

**12** is an air-stable, yellow crystalline salt. It is formed in approximately 90% yield in pure form under mild conditions (15 min at ambient temperature in $CH_2Cl_2$). The symmetrical structure of **12** follows (a) from $^{31}P$ NMR (a single absorption at −17.7 ppm vs. $H_3PO_4$), (b) from $^1H$ NMR (singlet at $\tau$ = 7.25), and (c) from IR, which shows an intense absorption at 1850 $cm^{-1}$. This latter value is about 100 $cm^{-1}$ lower than is customary for known allenes.[10]

**12** can be regarded as the first representative of bis geminally donor–acceptor substituted allenes **13**, a structural counterpart of push-pull allenes **14**, which have been known for some time.[14]



**13**



**14**

In order to obtain a deeper understanding of the bonding situation in **12**, both a theoretical and an X-ray structure investigation of this compound were undertaken, the results of which are described below.

**Crystal and Molecular Structure of 12.** In the crystal the dication and both anions are arranged in such a way that there are no contacts shorter than 400 pm between them. Obviously there are no significant interactions.

The bonding parameters of the allene moiety in **12** (C(1)–C(2) = 129 (3) pm, C(2)–C(3) = 132 (3) pm, C(1)–C(2)–C(3) = 177.5 (18)°) do not deviate significantly from theoretical values and from mean bond lengths and bond angles found in other allenes (130.9 pm in unsubstituted allene by electron diffraction,[12] 133 pm in methyl allene by microwave spectroscopy,[13] 130.7 pm and 178.1° in allene dicarboxylic acid by X-ray diffraction).[14] At the carbon atoms C(1) and C(3) the C(2)–C–N angles are slightly widened (127° and 125°) and C(2)–C–P and N–C–P are somewhat reduced.

C(1)–N(1) (136 (2) pm) and C(3)–N(2) (139 (2) pm) are of the same lengths as C–N bonds in bis- and tetrakis(dimethylamino)allyl cations,[15,16] indicating a similar degree of $\pi$-conjugation.

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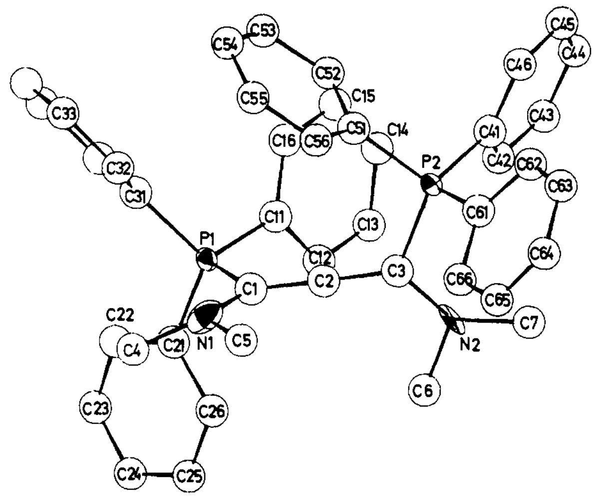
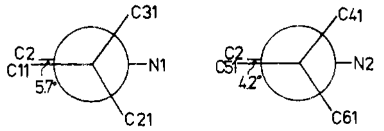


**Figure 1.** A perspective drawing of the dication of **12**. Hydrogen atoms and anions are omitted for clarity.

The nitrogen atoms in **12** are not exactly coplanar with the atoms bound to them: N(1) (N(2)) is located 15 pm (18 pm) above the plane of C(1), C(4), and C(5) (C(3), C(6) and C(7)). P(1)–C(1) and P(2)–C(3) bond lengths (183 (2) pm) are slightly longer than the P–$C_{sp^2(phenyl)}$ distances within the same molecule and are at the upper limit of values found in phosphonium ions (175–181 pm).[17] The arrangement of the substitutents along the P–$C_{allene}$ bonds is shown in the following Newman projections (view from P to $C_{allene}$).



Thus steric interactions between phenyl and amino groups are minimized. Enlargement of the angles C(21)–P(1)–C(31) (113.4 (7)°) and C(41)–P(2)–C(61) (113.3(7)°) could also be due to steric reasons.

Deviations from the ideal 90° allene twist[18] are not unusual. Apart from the NCCN and PCCP dihedrals of 98.7° and 95.5°, respectively, found for **12**, allenedicarboxylic acid is twisted by 93.3°. In carbodiimides, the structures of which should be allene-like, deviations up to 23.5° from the ideal 90° geometry have been found crystallographically.[19,20]

The best planes of the amino groups (N(1), C(1), C(4), C(5) and N(2), C(3), C(6), C(7)) are twisted against the planes N(1), C(1), P(1) (12.2°) and N(2), C(3), P(2) (9.4°). Stronger twisting should be unfavorable because of the steric interactions discussed before.

All deviations from an ideal geometry within the structure of **12** are not unusual. They either do not exceed standard deviations or are of a magnitude which can be caused by packing forces. However, electronic effects (see below) may also be responsible for the observed geometry distortions.

**The MO Theory of Gem Donor–Acceptor Allenes.** The structure and rotational behavior of a bis geminally donor–acceptor substituted allene such as **12** are of considerable theoretical interest, especially in comparison with push-pull allenes of type **14**. We have therefore carried out MNDO semiempirical molecular orbital calculations[21,22] on the model allene **15**. Full geometry optimization yielded the $C_2$ structure shown in Figure 2. As found in the X-ray structure of **12** the model compound adopts a transoid configuration, the angle between PPC planes being 103.9° and between NCC planes being 118.1° compared with 96.0° and 98.7°, respectively, found for **12**. The bond angle at $C_2$ is calculated to be 177.9°, compared with 177.5° found for **12**. The widening of the CCN angles (129.3° calculated for **15**, ca. 126° found for **12**) and the narrowing of the CCP angles (118.7° in **15**, ca. 117° in **12**) are also common features of the theoretical and experimental geometries. The major difference between the two structures is the theoretically predicted pyramidalization of $C_1$ and $C_3$, which is less pronounced in **12**. The pyramidalization at the nitrogen atoms in **12** is, however, reproduced by the calculations on **15**.

The close agreement between the structural deviations exhibited by **12** and those calculated for **15**, in which steric effects cannot be important, strongly suggests that the deformations are electronic in origin. The tendency to form a twisted structure can best be

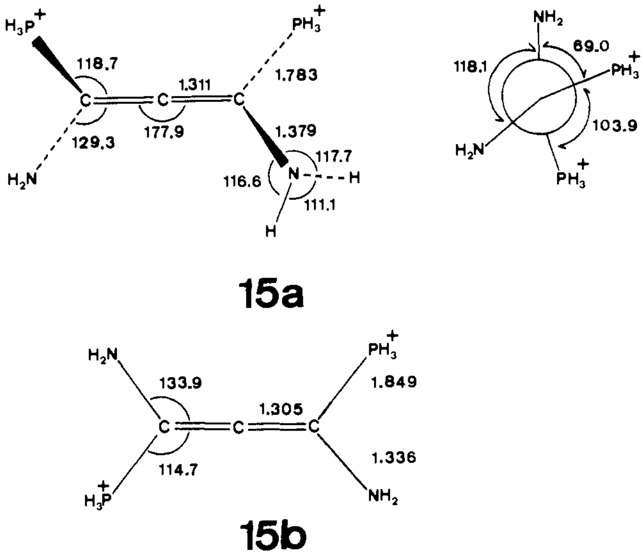


**Figure 2.** MNDO-optimized geometries of **15a** and **15b**. Bond lengths are in angstroms and angles in degrees.

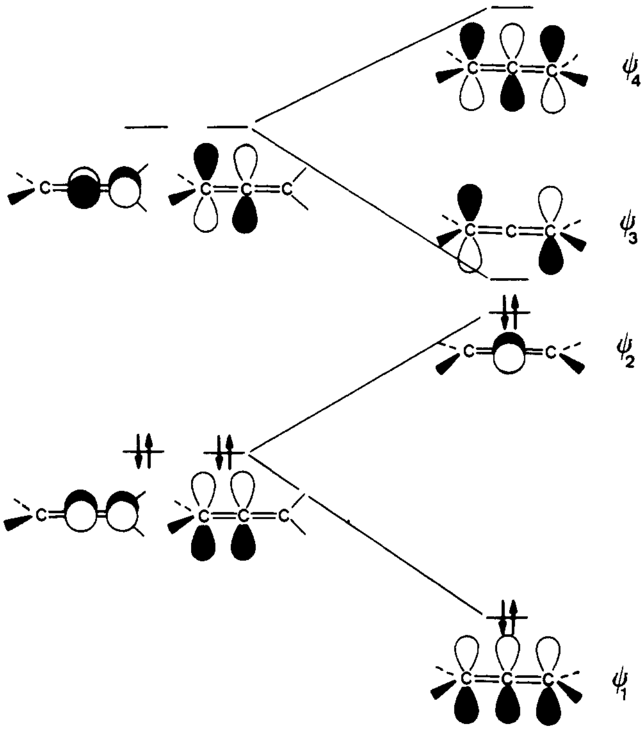


**Figure 3.** Correlation diagram for the $\pi$ orbitals on rotation from $D_{2d}$ to $D_{2h}$ alkene.

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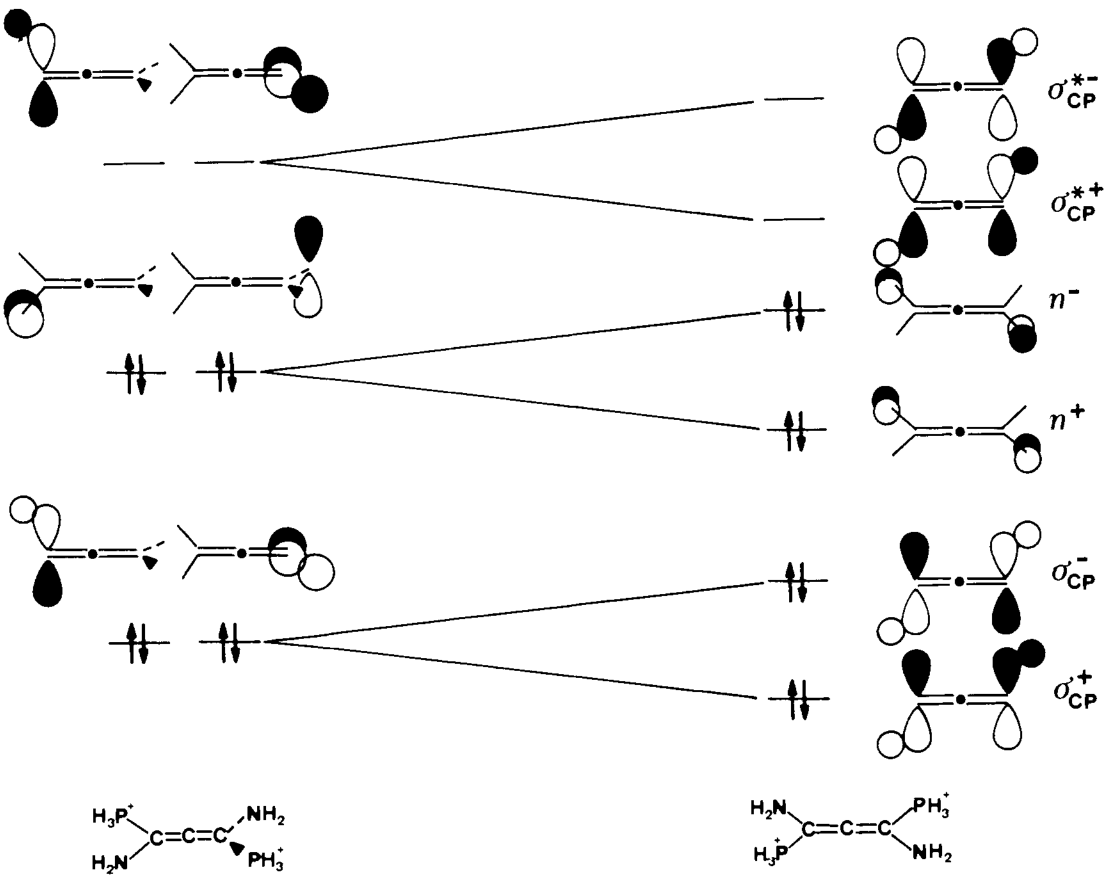

**Figure 4.** The $\sigma_{CP}$, $\sigma_{CP}$*, and nitrogen lone-pair orbitals for **15a** and **15b**.

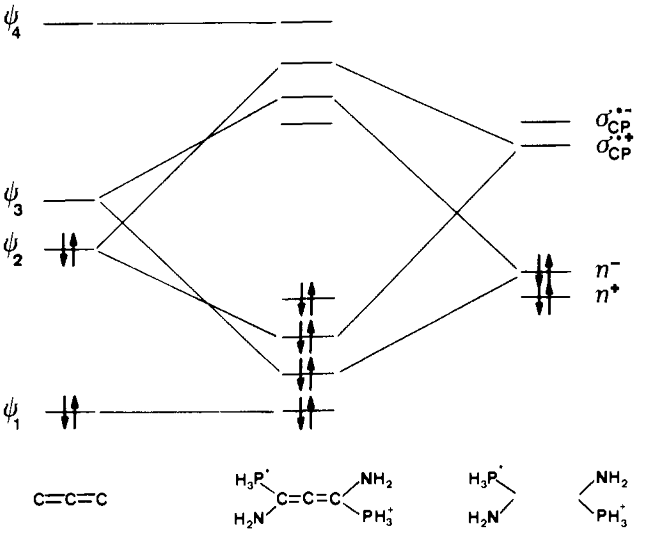

**Figure 5.** Interaction diagram for **15b**. The orbitals are labeled as in Figures 3 and 4.

understood by considering the MO interactions in perpendicular and planar **15** (**15a** and **15b**, respectively). Figure 3 shows the $\pi$ orbitals of $D_{2d}$ and $D_{2h}$ allene.[23] $\psi_2$ and $\psi_3$ in the planar form are nonbonding orbitals, so that the singlet planar allene is simultaneously a strong $\pi$ donor and a strong $\pi$ acceptor in perpendicular planes. Figure 4 shows the carbon-phosphorus $\sigma$ orbitals and the nitrogen lone pairs in **15a** and **15b**. Note that the low-lying $\sigma^*_{CP}$ orbitals in **15b** form a symmetrical in-plane $\pi$-acceptor orbital and that the nitrogen lone pairs form an unsymmetrical $\pi$-donor orbital. Figure 5 shows the interaction diagrams between the allene $\pi$ system and the donor-acceptor

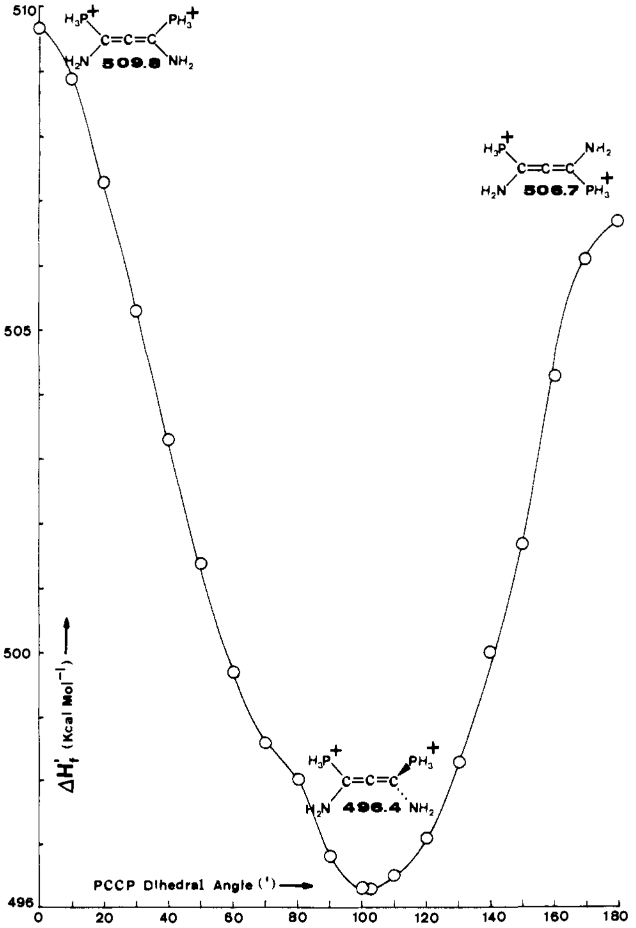

**Figure 6.** Rotational energy profile for **15**. The heats of formation (kcal mol$^{-1}$) of the stationary points are given below the structures.

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[23] See: Seeger, R.; Krishnan, R.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1977**, *99*, 7103.

Table II. Final Positional and Thermal Parameters for 12[a]

| atom | $x/a$ | $y/b$ | $z/c$ | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{13}$ | $B_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| I(1) | 0.8032 (1) | 0.09702 (6) | 0.09837 (6) | 3.57 (7) | 5.74 (7) | 5.87 (8) | −0.05 (6) | 0.95 (6) | 0.86 (6) |
| I(2) | 0.6120 (1) | 0.42779 (6) | 0.14685 (5) | 4.31 (7) | 5.23 (7) | 4.99 (7) | −0.27 (6) | 0.90 (5) | 0.30 (5) |
| P(1) | 0.0986 (4) | 0.2610 (2) | 0.4554 (2) | 2.6 (2) | 2.6 (2) | 3.3 (2) | −0.2 (2) | 0.7 (2) | −0.2 (2) |
| P(2) | 0.3189 (4) | 0.2608 (2) | 0.2881 (2) | 2.6 (2) | 2.4 (2) | 3.5 (2) | −0.1 (2) | 0.6 (2) | 0.1 (2) |
| C(1) | 0.217 (2) | 0.2000 (9) | 0.4309 (9) | 2.8 (10) | 2.9 (9) | 4.9 (11) | −0.4 (7) | 0.1 (8) | 1.1 (8) |
| C(2) | 0.210 (2) | 0.1983 (8) | 0.3739 (8) | 3.0 (8) | 2.1 (7) | 2.6 (8) | 0.4 (6) | 0.4 (6) | 0.2 (7) |
| C(3) | 0.208 (1) | 0.1975 (8) | 0.3158 (7) | 1.3 (8) | 3.1 (8) | 2.3 (8) | 0.6 (6) | 0.2 (7) | 0.1 (7) |
| N(1) | 0.303 (1) | 0.1614 (7) | 0.4741 (6) | 4.6 (9) | 4.1 (8) | 4.3 (8) | 2.2 (7) | 3.0 (7) | 0.2 (6) |
| C(4) | 0.284 (2) | 0.1429 (10) | 0.5319 (8) | 6.5 (12) | 6.5 (11) | 3.2 (10) | 2.9 (9) | 2.0 (9) | 1.4 (8) |
| C(5) | 0.399 (2) | 0.1130 (10) | 0.4539 (8) | 8.2 (14) | 5.0 (10) | 4.3 (10) | 1.2 (10) | 1.0 (10) | 0.4 (8) |
| N(2) | 0.123 (1) | 0.1547 (8) | 0.2733 (7) | 3.7 (8) | 4.3 (8) | 5.5 (9) | −1.8 (7) | 1.0 (7) | −1.9 (7) |
| C(6) | 0.044 (2) | 0.1007 (11) | 0.2966 (10) | 5.2 (12) | 6.8 (11) | 6.8 (12) | −4.9 (10) | 1.7 (9) | −1.6 (10) |
| C(7) | 0.140 (2) | 0.1366 (9) | 0.2150 (9) | 5.9 (12) | 3.8 (10) | 7.0 (13) | −1.6 (8) | 0.6 (10) | −1.6 (9) |

Phenyl Groups

| atom | $x/a$ | $y/b$ | $z/c$ | $10^4B$, pm$^2$ | atom | $x/a$ | $y/b$ | $z/c$ | $10^4B$, pm$^2$ |
|---|---|---|---|---|---|---|---|---|---|
| C(11) | 0.007 (2) | 0.3128 (8) | 0.3930 (7) | 3.1 (3) | C(41) | 0.228 (2) | 0.3252 (8) | 0.2326 (6) | 3.1 (3) |
| C(12) | −0.108 (2) | 0.2816 (9) | 0.3568 (8) | 4.7 (4) | C(42) | 0.091 (2) | 0.3233 (10) | 0.2204 (8) | 4.9 (4) |
| C(13) | −0.179 (2) | 0.3250 (10) | 0.3109 (8) | 5.4 (4) | C(43) | 0.023 (2) | 0.3725 (11) | 0.1778 (9) | 6.6 (5) |
| C(14) | −0.134 (2) | 0.3952 (10) | 0.3002 (8) | 5.5 (4) | C(44) | 0.085 (2) | 0.4240 (10) | 0.1515 (9) | 5.9 (5) |
| C(15) | −0.028 (2) | 0.4275 (9) | 0.3349 (8) | 4.4 (4) | C(45) | 0.218 (2) | 0.4289 (9) | 0.1665 (8) | 4.8 (4) |
| C(16) | 0.045 (2) | 0.3836 (8) | 0.3809 (6) | 3.3 (3) | C(46) | 0.292 (2) | 0.3786 (9) | 0.2067 (7) | 3.7 (4) |
| C(21) | −0.013 (2) | 0.2016 (8) | 0.4824 (7) | 3.1 (3) | C(51) | 0.409 (1) | 0.3146 (8) | 0.3484 (6) | 2.6 (2) |
| C(22) | −0.081 (2) | 0.2248 (9) | 0.5231 (7) | 4.1 (4) | C(52) | 0.364 (2) | 0.3852 (9) | 0.3602 (7) | 3.7 (4) |
| C(23) | −0.177 (2) | 0.1782 (9) | 0.5390 (8) | 4.7 (4) | C(53) | 0.436 (2) | 0.4260 (9) | 0.4108 (7) | 4.5 (4) |
| C(24) | −0.200 (2) | 0.1083 (10) | 0.5165 (8) | 5.3 (4) | C(54) | 0.549 (2) | 0.3971 (9) | 0.4459 (7) | 4.4 (4) |
| C(25) | −0.134 (2) | 0.0835 (11) | 0.4755 (10) | 7.3 (6) | C(55) | 0.592 (2) | 0.3274 (10) | 0.4337 (8) | 4.9 (4) |
| C(26) | −0.034 (2) | 0.1287 (10) | 0.4574 (8) | 5.2 (4) | C(56) | 0.526 (2) | 0.2856 (8) | 0.3853 (8) | 4.7 (4) |
| C(31) | 0.179 (2) | 0.3266 (8) | 0.5087 (7) | 3.2 (7) | C(61) | 0.433 (2) | 0.2044 (8) | 0.2606 (7) | 3.4 (3) |
| C(32) | 0.316 (2) | 0.3286 (9) | 0.5283 (8) | 4.6 (4) | C(62) | 0.506 (2) | 0.2308 (9) | 0.2205 (8) | 4.5 (4) |
| C(33) | 0.373 (2) | 0.3835 (10) | 0.5690 (8) | 5.8 (5) | C(63) | 0.598 (2) | 0.1854 (10) | 0.2045 (8) | 5.2 (4) |
| C(34) | 0.296 (2) | 0.4352 (10) | 0.5900 (8) | 5.6 (4) | C(64) | 0.616 (2) | 0.1138 (10) | 0.2246 (8) | 4.8 (4) |
| C(35) | 0.165 (2) | 0.4375 (10) | 0.5721 (8) | 5.0 (4) | C(65) | 0.545 (2) | 0.0864 (10) | 0.2612 (9) | 6.2 (5) |
| C(36) | 0.107 (2) | 0.3818 (9) | 0.5300 (7) | 4.3 (4) | C(66) | 0.455 (2) | 0.1306 (10) | 0.2829 (8) | 4.8 (4) |

Hydrogen Atoms

| atom | $x/a$ | $y/b$ | $z/c$ | atom | $x/a$ | $y/b$ | $z/c$ | atom | $x/a$ | $y/b$ | $z/c$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| H(12) | −0.138 | 0.231 | 0.364 | H(36) | 0.012 | 0.381 | 0.515 | H(65) | 0.547 | 0.032 | 0.267 |
| H(13) | −0.260 | 0.307 | 0.284 | H(42) | 0.042 | 0.282 | 0.233 | H(66) | 0.409 | 0.110 | 0.311 |
| H(14) | −0.183 | 0.426 | 0.266 | H(43) | −0.074 | 0.374 | 0.175 | H(411) | 0.322 | 0.168 | 0.568 |
| H(15) | 0.004 | 0.480 | 0.328 | H(44) | 0.033 | 0.458 | 0.121 | H(421) | 0.191 | 0.145 | 0.527 |
| H(16) | 0.125 | 0.404 | 0.405 | H(45) | 0.264 | 0.469 | 0.152 | H(431) | 0.310 | 0.091 | 0.537 |
| H(22) | −0.058 | 0.273 | 0.547 | H(46) | 0.387 | 0.381 | 0.218 | H(511) | 0.440 | 0.136 | 0.427 |
| H(23) | −0.231 | 0.197 | 0.566 | H(52) | 0.286 | 0.408 | 0.322 | H(521) | 0.473 | 0.100 | 0.491 |
| H(24) | −0.259 | 0.075 | 0.533 | H(53) | 0.404 | 0.476 | 0.421 | H(531) | 0.365 | 0.065 | 0.441 |
| H(25) | −0.153 | 0.034 | 0.456 | H(54) | 0.595 | 0.427 | 0.481 | H(611) | 0.101 | 0.059 | 0.318 |
| H(26) | 0.017 | 0.111 | 0.427 | H(55) | 0.674 | 0.307 | 0.459 | H(621) | 0.012 | 0.123 | 0.331 |
| H(32) | 0.371 | 0.292 | 0.510 | H(56) | 0.561 | 0.236 | 0.376 | H(631) | −0.026 | 0.080 | 0.271 |
| H(33) | 0.470 | 0.385 | 0.587 | H(62) | 0.488 | 0.281 | 0.206 | H(711) | 0.205 | 0.098 | 0.216 |
| H(34) | 0.338 | 0.476 | 0.620 | H(63) | 0.644 | 0.202 | 0.174 | H(721) | 0.061 | 0.117 | 0.187 |
| H(35) | 0.110 | 0.475 | 0.587 | H(64) | 0.693 | 0.084 | 0.222 | H(731) | 0.167 | 0.178 | 0.192 |

[a] In this table and those subsequent standard deviations in the least significant figure are given in parantheses. Anisotropic thermal parameters are in the form $\exp[-\frac{1}{4}(h^2a^{*2}B_{11} + k^2b^{*2}B_{22} + l^2c^{*2}B_{33} + 2hka^*b^*B_{12} + 2hla^*c^*B_{13} + 2klb^*c^*B_{23})]$; $B_{ij}$ in $10^4$ pm$^2$.

combinations in **15a** and **15b**. The planar allene is preferentially stabilized relative to its $D_{2d}$ rotamer by donation from $\psi_2$ to the symmetrical $\sigma^*_{CP}$ combination and by donation from the unsymmetrical nitrogen lone-pair combination to $\psi_3$. These interactions result in (a) a considerable lowering of the allene rotation barrier, (b) a tendency for the structure to twist away from the perpendicular conformation in order to gain donor–acceptor stabilization despite the inherent allene rotation barrier, (c) a tilt of the $NH_2CPH_3^+$ unit to optimize the overlap of the $\sigma^*_{CP}$ orbital with the allene $\pi$-donor orbitals (i.e., a narrowing of the CCP angles and a widening of the CCN angles), and (d) a shortening of the CN bond due to extra $\pi$ overlap and a lengthening of the CP bond due to donation to the $\sigma^*_{CP}$ orbital (negative hyperconjugation). The geometry of **15b** (Figure 2) confirms this analysis, the deformations all being more pronounced than those in **15a**. Note that the planar allene is almost linear. The MNDO-calculated rotation profile for **15** (Figure 6) shows barriers of 10.3 kcal mol$^{-1}$ via the trans form and 13.4 kcal mol$^{-1}$ via the cis form, compared with 60 kcal mol$^{-1}$ calculated by MNDO for singlet allene itself.[24]

The twisting and pyramidalization of the amino groups is also a consequence of the low-lying $\sigma^*_{CP}$ orbitals. The amino donors, having a choice between allene and carbon–phosphorus acceptor orbitals, adopt a compromise conformation in which they can interact with both types of acceptors.

## Experimental Section

**(A) Synthetic Work. HI Adduct of 1,3-Bis(dimethylamino)-1,3-diiodoallyl Diodide (7)** A stream of dry HI gas is bubbled through a solution of 5 g of **6** (21.6 mmol) in 50 mL of $CH_2Cl_2$. After some minutes **7** starts to precipitate as yellow crystals. The addition of HI is continued until no further precipitation can be observed. The product is filtered off, washed with dry ether, and dried in vacuo. Total yield: 12.4 g (91%) of analytically pure product with mp 151 °C dec. The product is air-stable but somewhat light-sensitive, changing gradually in color from light yellow to brown in diffuse daylight without noticeable consequences with regard to analytical composition or spectroscopic properties.

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(24) Kos, A. J.; Schleyer, P. v. R., unpublished results.

**Table III.** Selected Bond Distances (pm) and Angles (Deg) for 12

| | | | |
|---|---|---|---|
| C(1)–C(2) | 129 (3) | C(2)–C(3) | 132 (3) |
| C(1)–P(1) | 183 (2) | C(3)–P(2) | 183 (2) |
| P(1)–C(11) | 178 (2) | P(2)–C(41) | 180 (2) |
| P(1)–C(21) | 178 (2) | P(2)–C(51) | 177 (2) |
| P(1)–C(31) | 176 (2) | P(2)–C(61) | 177 (2) |
| C(1)–N(1) | 136 (2) | C(3)–N(2) | 139 (2) |
| N(1)–C(4) | 142 (2) | N(2)–C(6) | 144 (2) |
| N(1)–C(5) | 147 (2) | N(2)–C(7) | 142 (3) |
| C(1)–C(2)–C(3) | 177.5 (18) | | |
| C(2)–C(1)–P(1) | 115.8 (14) | C(2)–C(3)–P(2) | 118.5 (12) |
| C(2)–C(1)–N(1) | 127.0 (17) | C(2)–C(3)–N(2) | 125.0 (15) |
| P(1)–C(1)–N(1) | 117.1 (12) | N(2)–C(3)–P(2) | 116.5 (11) |
| C(1)–P(1)–C(11) | 109.6 (8) | C(3)–P(2)–C(41) | 111.0 (7) |
| C(1)–P(1)–C(21) | 107.6 (8) | C(3)–P(2)–C(51) | 109.1 (7) |
| C(1)–P(1)–C(31) | 110.5 (8) | C(3)–P(2)–C(61) | 107.9 (7) |
| C(11)–P(1)–C(21) | 108.1 (7) | C(41)–P(2)–C(51) | 108.2 (7) |
| C(11)–P(1)–C(31) | 107.6 (7) | C(41)–P(2)–C(61) | 113.3 (7) |
| C(21)–P(1)–C(31) | 113.4 (7) | C(51)–P(2)–C(61) | 107.3 (7) |
| C(1)–N(1)–C(4) | 125.9 (15) | C(3)–N(2)–C(6) | 115.7 (14) |
| C(1)–N(1)–C(5) | 116.6 (14) | C(3)–N(2)–C(7) | 126.0 (15) |
| C(4)–N(1)–C(5) | 114.1 (14) | C(6)–N(2)–C(7) | 113.7 (15) |

IR (KBr): 1615, 1515, 1410, 1280 cm$^{-1}$. Due to its insolubility no $^1$H NMR could be taken. Anal. Calcd for $C_7H_{14}I_4N_2$: C, 13.24; H, 2.21; N, 4.42. Found: C, 13.28; H, 2.17; N, 4.27.

**1,3-Bis(dimethylamino)-1,3-diiodoallyl Iodide (8).** To a suspension of 1.9 g (3 mmol) of salt **7** in 20 mL of $CH_2Cl_2$ 303 mg of $NEt_3$ in 5 mL of $CH_2Cl_2$ are added dropwise. After 2 h of stirring at ambient temperature the $CH_2Cl_2$-insoluble salt **8** is filtered off, washed several times with $CH_2Cl_2$, and dried in vacuo. Yield: 1.28 g (84%) of yellow crystals with mp 141–143 °C dec.

IR (KBr): 1520, 1415, 1370, 1280, 1110 cm$^{-1}$. Due to solubility problems no $^1$H NMR could be taken. Anal. Calcd for $C_7H_{13}I_3N_2$: C, 16.62; H, 2.59; N, 5.53. Found: C, 16.77; H, 2.57; N, 5.59.

**1,3-Bis(dimethylamino)-3-iodopropargyl Iodide (9).** A solution of 2.02 g (20 mmol) of $NEt_3$ in 20 mL of $CH_2Cl_2$ is added dropwise to a stirred suspension of 6.3 g of **8** in 50 mL of $CH_2Cl_2$. After complete addition of the base a clear solution is obtained. After 1 h ether is added until the product just starts to precipitate, and then the reaction mixture is kept at –20 °C overnight. Thus 3.13 g (83%) of yellow salt **9** is obtained in pure crystalline form (contaminations by $NEt_3H^+I^-$ were not observed under the workup conditions given). Yield: yellow needles from $CH_2Cl_2/Et_2O$ with mp 145 °C dec.

IR (KBr): 2155, 2158, 1620, 1375, 973 cm$^{-1}$. UV ($CH_3CN$): $\lambda_{max}$ = 328 mm (log $\epsilon$ = 4.71). $^1$H NMR ($CDCl_3$): $\delta$ 3.18 (s, 6 H), 3.58 (dc, 6 H). Anal. Calcd for $C_7H_{12}I_2N_2$: C, 22.24; H, 3.19; N, 7.41. Found: C, 22.30, H, 3.24; N, 7.46.

**1,3-Bis(dimethylamino)-1,3-Bis(triphenylphosphonio)allene Diiodide (12).** A solution of 1.13 g (3 mmol) of **9** in 25 mL of $CH_2Cl$ is added dropwise to a solution of 1.57 g (6 mmol) of triphenylphosphine in 25 mL of $CH_2Cl_2$. After 15 min at ambient temperature $Et_2O$ is added to the reddish solution and 2.4 g (89%) of yellow crystalline salt **12** can be precipitated. After crystallization from $CH_2Cl_2/Et_2O$ yellow needles with mp 130 °C dec are obtained, which gradually turn reddish brown in diffuse daylight.

IR (KBr): 1845, 1475, 1432, 1318, 1100, 1090 cm$^{-1}$. $^1$H NMR ($CDCl_3$): $\delta$ 2.7 (d, 12 H), 7.6 (mc, 30 H). $^{31}$P NMR ($CDCl_3$): $\delta$ –17.7 (vs, $H_3PO_4$). Anal. Calcd for $C_{43}H_{42}I_2N_2P_2$: C, 57.22; H, 4.69; N, 3.10. Found: C, 56.75; H, 4.55; N, 3.09.

**(B) Structure Determination and Refinement.** Crystals of **12** were obtained by slow evaporation of an acetonitrile solution. A crystal (0.3 × 0.3 × 0.3 mm) was mounted on a Syntex P2$_1$ automatic four-circle diffractometer equipped with a scintillation counter and a graphite monochromator. Mo K$\alpha$ radiation ($\lambda$ = 71.069 pm) was used for all measurements. Centering and refinement of 15 reflections from different parts of the reciprocal space resulted in the following unit-cell dimension: $a$ = 1046 (1) pm, $b$ = 1769 (3) pm, $c$ = 2287 (4) pm, $\beta$ = 103.1 (1)°, $V$ = 4122.10$^6$ pm$^3$, $d$(calcd) = 1.45 g/cm$^3$. Systematic absences were consistent with space group $P2_1/c$ ($Z$ = 4). Diffraction intensities were measured in an $\omega$-scan mode for which the scan range was 0.9°; the scan rate varied as a function of maximum peak intensity from 1.0 to 29.3 min$^{-1}$. Background radiation was measured on each side of the reflection center for half of the total scan time. A reference reflection measured every 50 reflections showed no significant deviation in its intensity. A total of 4530 independent reflections were collected ($2° \leq 2\theta \leq 43°$). Intensity data were corrected for Lorentz and polarization effects; absorption correction was not applied. The structure was solved by the heavy-atom method (Syntex XTL); positions of some hydrogen atoms were calculated according to the theoretical geometry. Atomic coordinates and temperature factors of the nonhydrogen atoms and a scale factor were refined by full-matrix least squares with 2901 structure factors ($F_o \geq 4.3\ \sigma(F^o)$). Hydrogens were included as fixed atom contributions ($B_{iso}$ = 5.0 pm$^2$). Final $R_1 = R_2 = 0.076$, where $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2}$ ($1/w = \sigma^2(F_o{}' + 0.000\,14F_o{}^2$. Table I, the observed and calculated structure factors, is available as supplementary material. The final positional and thermal parameters are listed in Table II. Table III contains interatomic bond lengths and angles.

## Conclusion

The calculated and experimentally observed structural features of **12** clearly demonstrate that the triphenylphosponio group in **13** acts solely as a $\sigma$-acceptor, not as a $\pi$-acceptor.

The latent dissociation of both triphenylphosphine moieties to give **16** according to (2) is reflected both in the experimental structure of **12** and in the corresponding model calculation.

$$\mathbf{12} \rightarrow \underset{\mathbf{16}}{R_2N^+{=}C{=}C{=}C{=}^+NR_2} + 2P(Ph)_3 \qquad (2)$$

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**Supplementary Material Available:** Table I, observed and calculated structure factors for **12** (21 pages). Ordering information is given on any current masthead page.