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Polarity of $^3\lambda^5$ -Phosphoranes

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POLARITY OF σ^3, λ^5 -PHOSPHORANES

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Tricoordinated pentavalent phosphorus compounds - σ^3, λ^5 -
 -phosphoranes - present a new field in unusually (low)
 coordinated phosphorus chemistry. Our current interest in
 these compounds is stimulated by the possibility of actual
 determination of unknown phosphorus bond polarities, using
 electrical methods in subsequent investigations of the
 spatial and electronic structure of σ^3, λ^5 -phosphoranes.
 We have studied the series of bis(imino)phosphoranes by the
 method of dipole moments $R^2N=P(R^1)=NR^3$ (I-VI) R^1, R^2, R^3 ,
 $\mu_{exp. (D)}$: (I) $N(SiMe_3)_2, SiMe_3, SiMe_3$, 2.16; (II) $N(SiMe_3)_2$,
 $t-Bu, t-Bu$, 2.36; (III) $N(SiMe_3)_2, SiMe_3, t-Bu$, 2.26; (IV)
 $2,4,6-Me_3C_6H_2, t-Bu, 2,4,6-t-Bu_3C_6H_2$, 2.44; (V)
 $t-Bu(Me_3Si)N, t-Bu, t-Bu$, 2.74; (VI) $c-2,2,6,6-Me_4C_5H_6N$,
 $SiMe_3, SiMe_3$, 2.82 and defined $P=N$ bond polarity (3.14D).
 Dipole moments (I-VI) are described by the given values,
 the group moments $R-P$ and $R-N$ were previously found from
 dicoordinated phosphorus compounds. The tendency of in-
 creasing $\mu_{exp. 1}$ with the growth of n, π -donor abilities of
 substituent R^1 in row (I-III)-(V)-(VI) is possibly caused
 by the increase of the conjugative effect contribution in
 stabilization of the 4-electron 3-centre Π -system $N=P=N$.