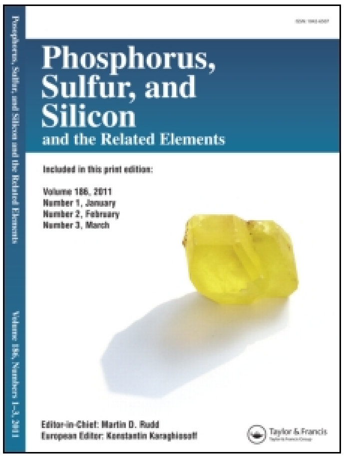

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Substituent Effects in Alpha-Amino and Hydroxyphosphonates Addition to Substituted Arylisocyanates: Theoretical Investigation

Roustem D. Saiakhov[a][b]; Albert R. Magafurov[b]; Vladimir I. Galkin[b]; Rafael A. Cherkasov[b]
[a] Department of Chemistry, Case Western Reserve University, Cleveland, OH, USA [b] Deportment of Chemistry, Kazan State University, Kazan, Russia

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Substituent Effects in Alpha-Amino and Hydroxyphosphonates Addition to Substituted Arylisocyanates: Theoretical Investigation

ROUSTEM D. SAIAKHOV[ab], ALBERT R. MAGAFUROV[b],
VLADIMIR I. GALKIN[b] and RAFAEL A. CHERKASOV[b]

[a]*Department of Chemistry, Case Western Reserve University,Cleveland OH 44106–7078, USA and* [b]*Department of Chemistry, Kazan State University, Kazan, 420008 Tatarstan, Russia*

Previously we have found [1] the possibility of the mechanism alteration for addition of aminophosphonate $(iPrO)_2P(O)CH_2NHBu$ and hydroxyphosphonate (HexO)2P(O)CH2OH to substituted arylisocyanates XC_6H_4NCO. The alteration seems to be dependent on the nature of substituents in the isocyanates. We have performed the investigation of MO energy and distribution in the both phosphonates and all isocyanates by AM1 methods using HyperChem molecular modeling program. From results of our calculations of HOMO and LUMO energy and distribution, not charge control but MO control governs that reaction. Introducing electronodonating substituent to aromatic ring of arylisocyanate increases the HOMO density of the nitrogen in NCO group, that makes Ad_E mechanism possible. However this alteration can be observed only for weak nucleophiles with low-energy HOMO – like hydroxyphosphonates. A possibility of HOMO(isocyanate)-LUMO(phosphonate) interaction has been shown for these compounds.

References

[1] A.R. Magafurov, R.D. Saiakhov, V.I. Galkin, R.A. Cherkasov, in *Abstracts of ICCPC XI*, Kazan, Russia, 1996, P.210.