

## electronic effect of substituents: symbols and signs

The inductive effect has universally been represented by the symbol I. This is now commonly taken to include both through-bonds and through-space transmission, but I is also used specifically for through-bonds transmission; through-space transmission is then symbolized as F (for field effect). The symbols for the influence of substituents exerted through electron delocalization have variously been M (mesomeric), E (electromeric), T (tautomeric), C (conjugative), K (konjugativ) and R (resonance). Since the present fashion is to use the term resonance effect, R is the most commonly used symbol, although M is still seen quite often. Both the possible sign conventions are in use. The Ingold sign convention associates electronegativity (relative to hydrogen atom) with a negative sign, electropositivity with a positive sign. Thus the nitro group is described as electronwithdrawing by virtue of its  $-I$  and  $-M$  effects; chloro is described as a  $-I$ ,  $+M$  substituent, etc. For correlation analysis and linear free-energy relationships this convention has been found inconvenient, for it is in contradiction to the sign convention for polar substituent constants ( $\sigma$ -constants). Authors concerned with these fields often avoid this contradiction by adopting the opposite sign convention originally associated with Robinson, for electronic effects. This practice is almost always associated with the use of R for the electron delocalization effect: thus the nitro group is a  $+I$ ,  $+R$  substituent; chloro a  $+I$ ,  $-R$  substituent, etc.

### **Source:**

PAC, 1994, 66, 1077 (*Glossary of terms used in physical organic chemistry (IUPAC Recommendations 1994)*) on page 1111